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THE ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS

AZARIAH T. LINCOLN

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THE ELECTRICAL CONDUCTIVITY

OF

NON-AQUEOUS SOLUTIONS

BY

AZARIAH THOMAS LINCOLN

A Thesis Submitted for the Degree of Doctor of Philosophy
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THE ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS.[1]

AZARIAH THOMAS LINCOLN, PH. D.
University of Wisconsin.

WITH PLATES II TO VII.

INTRODUCTION.

Van't Hoff formulated his modern theory of solutions from the results of Pfeffer's[2] classic experiments on the osmotic pressure of a few substances in aqueous solutions, and from the work of de Vries[3] who pointed out that equimolecular quantities of dissolved substances produce the same osmotic pressure. Van't Hoff[4] stated that the condition of a substance in the gaseous state is analogous to the condition in which a substance exists in dilute solutions wherein the osmotic pressure of the dissolved substance corresponds to the pressure of the gaseous particles. It was soon observed, however, that many substances did not give normal values for the osmotic pressure, the rise of the boiling, or lowering of the freezing point; and thus that the laws of gases would not hold for solutions of these substances.

Arrhenius pointed out that those substances which yield solutions in water that conduct electricity are acids, bases, and salts (called electrolytes); and that they are the same class of compounds as give abnormal values for the osmotic pressure, the rise of the boiling point, and the lowering of the freezing point in aqueous solutions. In order to explain these anomalous results, Arrhenius[1] promulgated his well known theory of electrolytic dissociation, which has been very widely accepted. The theory has, however, met with very strong opposition particularly from the English chemists. Some English scientists contend that the supposition that the molecules of the dissolved substance are electrolytically dissociated is not necessary to explain the facts, and that in many cases it is not adequate. However, the dissociation theory has stimulated the investigation of aqueous solutions and particularly as to their electrical conductivity. Attention has also been directed to the study of mixtures of water with other solvents, and more recently the attention of scientists has been directed towards the character of solutions other than aqueous. The investigation of non-aqueous solutions is replete with interest, and many lines of research, both theoretical and practical, offer themselves, the interdependence of which is very apparent. But the present research is confined chiefly to the electrical conductivity of non-aqueous solutions.

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[1] A thesis submitted for the degree of Doctor of Philosophy, University of Wisconsin, 1899.

[2] *Osmotische Untersuchungen*, Leipzig, 1877.

[3] *Zeit. phys. Chem.* 2, 414; 1888.

[4] *Zeit. phys. Chem.* 1, 481; 1887.

The degree of dissociation in aqueous solutions is calculated from determinations of the electrical conductivity and also from he rise of the boiling point and the lowering of the freezing point of the solutions; and the results show very close agreement. Hence in connection with the conductivity measurements of non-aqueous solutions, it is desirable to have boiling point and cryscopic determinations to aid in ascertaining the molecular condition of the dissolved substance. Since these methods are employed to determine to what extent the dissociation has taken place in aqueous solutions, one would naturally be inclined to apply them to solutions other than aqueous; for it is reasonable to suppose that the methods are as applicable to one solvent as to another. The advocates of the electrolytic dissociation theory state that whenever any solvent conducts electricity the dissolved substance is dissociated electrolytically, and consequently the solvent possesses dissociative power. This meaning of the term, dissociative power, will be retained throughout this paper. The agreement between the values for the degree of dissociation in non-aqueous solutions as calculated from the boiling point or the cryscopic, and from the conductivity determinations, is not nearly as close as in the case of aqueous solutions. In many cases the boiling point determinations show practically no dissociation, while the solution conducts well. It must be remembered, however, that a slight amount of dissociation cannot be detected by the boiling point method; and where the conductivity is slight, the dissociation might be sufficient to account for it. However, this difficulty would not be experienced in solutions that conduct well. Since these methods are used to determine the degree of dissociation and the results show so slight an agreement in non-aqueous solutions, it seems but proper to ask which of these methods shows the correct degree of dissociation; and one might further ask which of the methods is a measure of the dissociative power of the solvent.

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[1] *Zeit. phys. Chem.* **1**, 631; 1887.

A number of auxiliary theories have been advanced to explain many of the facts observed in relation to the conductivity of non-aqueous solutions. Nernst[1] calls attention to the fact that solvents which conduct electricity have a high specific inductive capacity. Brühl[2] concludes that the dissociative power of solvents is dependent upon spare valences; that is, the solvents that yield solutions which conduct, are unsaturated compounds. Dutoit and Aston[3] claim that only those solvents the molecules of which are polymerized, yield conducting solutions. Abegg points out that even these theories are not sufficient to explain satisfactorily the phenomenon of the electrical conductivity of non-aqueous solutions. These theories will be discussed more fully subsequently.

In face of the data that have been collected, and in view of the fact that such a large number of chemists to-day do not accept the electrolytic dissociation theory as applied to aqueous solutions, one may well hesitate to apply this theory to non-aqueous solutions, until there is a sufficiently firm experimental basis to justify it. The chief object of this investigation is therefore, to determine to what extent Arrhenius' theory, which is based upon the behavior of electrolytes in aqueous solutions, can be applied to the solutions that are non-aqueous. In presenting the results of this investigation, an inquiry will also be made as to whether there is any relation existing between the dissociative power of solvents and their other general properties.

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[1] *Zeit. phys. Chem.* **14**, 622; 1894.

[2] *Zeit. phys. Chem.* **18**, 514; 1895; **27**, 317; 1898; *Ber. Chem. Ges.*, Berlin **30**, 162; 1897.

[3] *Comptes rendus*, **125**, 240; 1897.

EXPERIMENTAL PART.

Qualitative Determinations.

In an investigation of the electrical conductivity of non-aqueous solutions, the chief requirement is that both the solvents and the dissolved substances be absolutely free from water. To accomplish this is not an easy task. Then, too, the question arises as to what anhydrous salts are soluble in the various solvents. In many cases this could only be answered by experiment. The work of other investigators on the conductivity of non-aqueous solutions has been confined almost exclusively to the salts of the alkalies, ammonium and the substituted ammonias. It was soon learned by direct experiment that the chlorides of many of the heavy metals are soluble in a number of organic solvents and that the solutions formed conduct electricity. Therefore the investigation was confined chiefly to the conductivity of the solutions of the salts (mostly chlorides) of the heavy metals. Even when the salts were readily soluble, conducting solutions were not always obtained. In order to determine what solutions conduct and to estimate roughly, at least, the relative magnitude of the conductivity, it was necessary to perform an elaborate series of qualitative experiments to ascertain what solvents yield solutions having a conductivity sufficient to justify quantitative measurements.

The method employed in making the qualitative determinations was as follows: Into a resistance cell of the Arrhenius pattern, the electrodes of which were about three millimeters apart, was introduced the solution to be tested. This cell, a rheostat, and a delicate galvanometer were placed in the circuit of a Leclanché element. The circuit was then completed and the deflection of the galvanometer needle noted. It was very seldom that any resistence had to be introduced by means of the rheostat. A hundredth normal solution of sulphuric acid gave a deflection of about twenty divisions when 500 ohms resistance was introduced. By means of a direct current thus employed polarization of course could not be avoided. The circuit was only closed for a few seconds. The sole object of these experiments being to ascertain whether the solution conducted, and to determine only very roughly the relative magnitude, the slight amount of polarization could be entirely neglected.

The solvents were all of the C. P. variety of standard makes: Kahlbaum, Merck, Schuchardt, or Trommsdorff. Professor Kremers of the pharmacy department of this university kindly furnished several compounds from his collection and Professor Hillyer kindly placed at my disposal a number of solvents in his possession. For thus furthering the experimental work, I desire to extend to these gentlemen my thanks. The methods employed in rectifying and dehydrating these solvents will be found under the head of the particular solvent in the record of the quantitative determinations.

The salts employed were absolutely anhydrous and the method employed in their preparation and dehydration will now be given.

Ferric chloride was prepared by passing anhydrous chlorine over heated iron wire contained in a hard glass tube. The chlorine was prepared in the usual manner from manganese dioxide and hydrochloric acid. The gas was conducted through a wash bottle containing water to free it from hydrochloric acid, then through sulphuric acid, then through a cylinder containing fused calcium chloride, and finally through another wash bottle containing sulphuric acid. From this it was conducted into the long hard glass tube containing the fine iron wire. This tube was gently warmed, and by increased heat the chloride was sublimed along the tube. This resublimation was repeated several times, and then the tube was sealed off and the product preserved in these sealed tubes. Before using, the tube was opened and allowed to remain under a bell jar containing concentrated sulphuric acid for several days, when not the least trace of free chlorine could be detected in the salt.

The trichloride of antimony was obtained by passing anhydrous chlorine over metallic antimony contained in a retort which was gently warmed. The chlorine was dried in the manner described above. The product was then distilled and this distillate redistilled, during which process all necessary precautions to exclude the moisture of the air were observed.

The cupric chloride was prepared in a manner analogous to that employed in the preparation of the chloride of iron.

Stannous and aluminium chlorides were prepared by passing dry hydrochloric acid gas over the respective metals which were contained in hard glass tubes. The hydrochloric acid gas was prepared by dropping concentrated hydrochloric acid into concentrated sulphuric acid, and then drying it by passing the gas through a train consisting of three bottles containing concentrated sulphuric acid and a cylinder filled with fused calcium chloride.

The trichloride of bismuth was prepared by Professor Kahlenberg by treating the hydroxide of bismuth with concentrated hydrochloric acid, evaporating the solution to a thick paste and thus volatilizing a large portion of the excess of the hydrochloric acid. The residue after cooling was finally broken up and tranferred to a Berlin porcelain retort and purified by distillation.

These chlorides were all pure and perfectly anhydrous; and every precaution necessary to keep them so was employed.

Arsenic trichloride was prepared by treating arsenious acid with dry hydrochloric acid gas in a retort and then distilling the product. This distillate was redistilled, and had a very constant boiling point.

The stannic chloride used was an anhydrous product from Schuchardt. The phosphorus trichloride from Kahlbaum was redistilled and that portion taken that gave a constant boiling point.

A C. P. sample of manganous chloride from Merck was recrystallized several times and then heated for several days in an air bath at a temperature of about 100° C. It was then thoroughly pulverized in a mortar and returned to the bath, where it remained for about two days longer. C. P.

samples of the chlorides of nickel and cadmium from Schuchardt were dehydrated in a similar manner. The C. P. sample of cobaltic chloride from Trommsdorff was treated in the manner just described; but the temperature was raised to about 120° C. for several hours. The C. P. samples of lead nitrate and mercuric iodide from Merck, mercuric cyanide from Trommsdorff, and zinc chloride from Kahlbaum were dehydrated, in the manner described above, at a temperature not exceeding 100° C. The silver cyanide was prepared from potassium cyanide and silver nitrate by Professor Kahlenberg, who dehydrated it and upon subsequent analysis found it to be pure.

During the course of the qualitative experiments a great many interesting facts relative to the solubility, color of solutions, etc., were brought out, to most of which it will not be possible to call attention at the present time. It was soon observed that if ferric chloride did not yield solutions that conducted electricity, it was not worth while to make tests with certain other salts; and for this reason many blank spaces occur in the following table. In each case the conductivity of the solvent was tested and the deflection of the galvanometer needle noted. In nearly all cases it was found that the solvents were excellent insulators, giving no deflection of the needle whatever. In the case of acetic aldehyde, furfurol, and ethylene glycol, the deflection was several divisions. When the salts were found to be quite soluble, the solutions were prepared in the resistance cell; but they were usually made up in small test tubes and frequently by the aid of heat. The strength of the solutions was not determined accurately; but it varied, being as high as five per cent. in some cases.

The electrolytic dissociative power of a solvent is believed by the supporters of the dissociation theory to be measured by the conductivity of its solutions. Since the qualitative determinations throw some light upon the dissociative power of solvents, the results are given in Table I. In the first two columns are given the names and formulæ of the solvent. In the next twenty-two columns is indicated whether the solutions of the several salts whose formulæ head the respective columns conduct electricity. Where the solution conducted so poorly that no deflection of the galvanometer needle was observed, the fact is indicated by the minus sign (—). The plus sign (+) indicates that the solution did conduct. The addition of the interrogative sign to the plus sign (+ ?) indicates that a very slight movement of the needle was detected; and when the plus sign is followed by the exclamation mark (+ !), this indicates that the solution conducts sufficiently well to make a quantitative determination desirable. The magnitude of the conductivity can be learned from the quantitative results given subsequently. Blank spaces indicate that determinations were not made, and the letter *i* indicates that the salt was insoluble in the solvent or very difficultly soluble. In the last two columns respectively, are given the dielectric constants and the coefficients of association of the solvents. The data in these two columns are as complete as could be obtained from the literature.[1]

The letters R & S refer to the article by Ramsay and Shields as authority;[2] R & A to the work of Ramsay and Aston;[3] and D & F to that of Dutoit and Friderich.[4] The letter V designates determinations by Vollmer, C by Carrara, D & A by Dutoit and Aston, and S by Schlamp.

From Table I it will be observed that ferric chloride dissolves in the hydrocarbons and their halogen substitution products, but the resulting solutions do not conduct. This is in harmony with what other investigators[5] have found concerning solutions of other salts in these solvents. It will be noted that both the dielectric constants and the coefficients of association (as far as they were available) are very low. The acid chlorides, acetyl and benzoyl chlorides, yield solutions of ferric chloride and antimony trichloride that do conduct. The coefficient of association in the case of acetyl chloride is about unity, thus showing no polymerization and the dielectric constant (the results of Drude and Thwing differ greatly) is much

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[1] (1) Thwing, *Zeit. phys. Chem.* **14**, 286; 1894.

(2) Drude, *Zeit. phys. Chem.* **23**, 308; 1897.

[2] Ramsay and Shields, *Jour. Chem. Soc.* **63**, 1089; 1893.

[3] Ramsay and Aston, *Jour. Chem. Soc.* **65**, 168; 1894.

[4] Dutoit and Friderich, *Bull. Chim. Soc. Paris* (3) **19**, 321; 1898.

[5] Kablukoff, *Jour. Russ. Chem. Soc.* **23**, 391; 1893. (Ref.) *Jour. Chem. Soc.* **64**, ii. 151; 1893.

HgI_2	$AgNO_3$	AgCN	KCl	LiCl	Dielectric constant (air = 1)	Coefficient of association.	
							1
					2.30 Landolt & Jahn	0.96 R & S (Schiff)	2
					2.3377 Palaz	1.01 R & S	3
					2.3648 "		4
					2.2758 Negreano		5
					2.47 "		6
							7
					3.95 Thwing	0.94 R & S (Eötvös	8
					2.2 Tereschin	1.01 R & S	9
							10
							11
						0.95 R & S (Eötvös)	12
							13
							14
							15
							16
					25.3 Thwing 15.4 Drude	1.06 R & S	17
							18
				V	32.65 Tereschin	3.43 R & S	19
	V			V	25.7 Rosa	2.74 R & S	20
				S	20.8 Thwing	2.25 R & S	21
	+ !			+ !	21.6 Thwing	1.88 R & S	22

its solutions conduct slightly — compare with chloral. The monochloracetate, the cyanacetate and the acetoacetate of ethyl all yield solutions that conduct well. The high dielectric constant of the last two will be noted as well as the coefficient of association of the last, which indicates that its molecules are not polymerized. In ethyl monochloracetate $AgNO_3$ is not soluble, while in the cyanacetate it dissolves readily, and the resulting solution conducts well. The electical conductivity of solutions in propyl acetate, butyl acetate and ethyl benzoate is very slight, and it will be noticed that the dielectric constants of these solvents are also low. Propyl propionate solutions conducted very little and in the case of amyl butyrate and amyl valerianate only slight deflections of the galvanometer needle were observed. It is probable that the dielectric constants of these esters are very low. Ethyl oxalate solutions conduct; but those of ethyl carbonate do not, notwithstanding the high oxygen content of this solvent, while ethyl chlorcarbonate yields solutions that conduct very well.

The class of organic solvents containing nitrogen are of particular interest. It will be noticed that ethyl nitrate, amyl nitrite, nitrobenzene, nitrotoluene, benzonitrile and pyridine yield solutions that conduct fairly well (See quantitative determinations). The dielectric constants of these solvents that have been determined would tend to indicate that their solutions would conduct. According to the association coefficients as determined by Ramsay and Shields the molecules of nitrobenzene, benzonitrile and pyridine are not polymerized. The solutions of ferric chloride in aniline, methylaniline and dimethylaniline conduct very poorly, whereas benzylamine appears to conduct slightly better.

In the toluidines ferric chloride is difficultly soluble and only a very slight movement of the galvanometer needle was observed. In xylidine most of the salts were insoluble; but silver nitrate dissolved quite readily and conducted fairly well, and the same was found to be the case in aniline. The dielectric constant for aniline is low, and the coefficient of association shows very slight polymerization. Phenylhydrazine dissolves ferric chloride readily, but not the slightest movement of the needle could be detected. Dutoit and Friderich[1] have shown that the nitriles conduct and the results given in this table shows that benzonitrile is not an exception. The dielectric constant would indicate this; and according to the determinations of Ramsay and Shields, as well as according to those of Traube, the molecules of this solvent are not polymerized. The solubility of the salts tested in piperidine is very slight except mercuric chloride and silver nitrate, and even these do not yield solutions that conduct very well. Quinoline yields solutions that conduct, but its molecules are not polymerized. The solution of ferric chloride in carbon disulphide did not conduct, nor should we expect it to do so from its low dielectric constant. Phosphorus trichloride does not yield solutions that conduct. Arsenic trichloride and mercuric chloride are very soluble in it, yet there was not the least movement of the needle. The solutions of ferric chloride and mercuric chloride in arsenic trichloride conduct very well.

In addition to the results tabulated in Table I it was found that stannic chloride dissolved in arsenic trichloride does not conduct, and the same was true of phosphorus trichloride. When phosphorus trichloride was added to a solution of mercuric chloride in arsenic trichloride, the conductivity was decreased to such an extent that the galvanometer needle did not even move. Further, a large number of other tests were made which were too detailed and numerous to include in these tabulated results. Suffice it to say, however, that of the very large number of tests made, both of organic and inorganic substances in these numerous solvents, there was not one instance where the solution conducted electricity, that the dissolved substance was not an acid, a base, or a salt.

Quantitative Determinations.

The method of Kohlrausch was employed in measuring the electrical conductivity — the resistance cell of the Arrhenius pattern being used. This cell was provided with a tightly fitting cover and the electrodes were about three millimeters apart. The determinations were made at 25° C. unless otherwise indicated, and the results are expressed in reciprocal mercury units. The higher temperature at which the conductivity was measured was obtained by heating the resistance cell and its contents in a paraffin bath. Owing to the small quantity of the solvents available in most cases it was not possible to make the dilutions in the ordinary manner. Five or ten cubic centimeters of the solvent were introduced into the resistance cell by means of a carefully calibrated burette, the conductivity was determined, and then weighed portions of the salt were successively introduced and the conductivity determinations made after each addition.

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[1] Loc. cit.

In the following tables of the electrical conductivity v represents the volume in liters in which one gram-molecule is contained and μ the molecular conductivity. Although the conductivity of the solvent has been determined in each case, it has not been deducted.

METHYL ALCOHOL.

The sample of methyl alcohol employed was dehydrated several times with anhydrous copper sulphate, over which it remained several days and from which it was decanted and distilled each time. The distillate was then treated with metallic sodium and again distilled. This distillate was fractionated twice, when a product with a very constant boiling point was obtained. The resistance was so great that the conductivity of the alcohol could be practically neglected. After standing for nine months the specific conductivity had decreased to only 5.7×10^{-6}.

TABLE II.

Solvent: methyl alcohol.

Ferric Chloride, $Fe Cl_3$.		Antimony Trichloride, $Sb Cl_3$.	
v	μ	v	μ
3.20	20.81	8.15	15.68
6.41	25.26	16.31	18.94
12.81	31.09	32.62	28.52
25.62	40.90	65.24	43.32
51.24	49.00	130.48	63.33
102.48	60.55	260.96	89.47
204.96	72.61	521.91	118.34
409.91	89.11	1,043.83	156.32
819.83	111.08		
1,639.66	147.08		

ETHYL ALCOHOL.

A sample of absolute alcohol was treated with anhydrous copper sulphate, over which it remained for several days. From this sulphate it was distilled, and the distillate was treated in the same manner as the original portion. The distillate from this was then treated with metallic sodium and then distilled. The distillate was redistilled twice; it boiled constantly at 76.8° at 749 mm. pressure. The specific conductivity was 7.7×10^{-7}.

TABLE III.

Solvent: ethyl alcohol.

Ferric chloride, $Fe Cl_3$.		Antimony Trichloride, $Sb Cl_3$.	
v	μ	v	μ
2.89	9.91	8.11	4.18
5.79	13.06	16.23	5.68
11.57	13.70	32.45	7.94
23.14	14.50	64.91	12.30
46.28	15.51	129.81	18.23
92.56	16.69	259.62	29.43
195.12	19.33		
390.24	21.20		

ALLYL ALCOHOL.

A C. P. sample of allyl alcohol from Merck was treated with K_2CO_3, over which it stood for several days. From this it was distilled and the distillate treated with fused potassium hydroxide. The distillate from this was again treated with caustic potash in contact with which it stood several days and then distilled. This distillate was redistilled twice and the conductivity determinations made as soon as possible. The specific conductivity was 6.5×10^{-6}.

TABLE IV.

Solvent: allyl alcohol.

Ferric Chloride, Fe Cl_3. v	μ
20.02	17.42
53.71	23.03
115.60	32.15

Ferric Chloride, (v = 20.02 at 25° C.) t	μ
25°	17.42
50	34.62
73	43.63
80	45.65

BENZYL ALCOHOL.

The sample of benzyl alcohol employed was from Merck and was rectified by distillation. The portion used had a very constant boiling point. Owing to the difficult solubility of the salts and the slight conductivity of solutions of this solvent very few determinations were made. The specific conductivity was 1.76×10^{-6}.

TABLE V.

Solvent: benzyl alcohol.

Ferric Chloride, Fe Cl_3. v	μ
88.06	2.62
895.22	6.31

Ferric Chloride, (v = 88.06 at 25° C.) t	μ
25°	2.62
54	5.08
85	6.46
100	7.19

PARALDEHYDE.

The sample of paraldehyde from Kahlbaum was redistilled and the portion coming over at a very constant temperature was employed. The specific conductivity was less than 3.4×10^{-7}.

TABLE VI.

Solvent: paraldehyde.

Ferric Chloride, $Fe\,Cl_3$.

v	μ
4.37	9.81
21.32	16.91
42.52	18.76
81.88	19.16
183.11	16.51
575.50	16.91

Antimony Trichloride, $Sb\,Cl_3$.

v	μ
5.57	0.202
20.76	0.356
61.16	0.532

Antimony Trichloride, (v = 5.57 at 25° C.)

t	μ
25.2°	0.295
26.6	0.299
29.0	0.298
32.0	0.295

BENZALDEHYDE.

The sample of benzaldehyde employed was from Schuchardt. It was purified by redistillation, and the portion boiling between 177° and 178° C. at 741.5 mm. pressure was used in the following determinations. The specific conductivity was less than 4.5×10^{-7}.

TABLE VII.

Solvent: benzaldehyde.

Ferric Chloride, $Fe\,Cl_3$.

v	μ
25.58	14.32
51.65	14.58
117.91	13.05
157.80	12.14
237.14	10.50

Antimony Trichloride, $Sb\,Cl_3$.

v	μ
1.96	0.12
2.42	0.14
3.51	0.18
5.80	0.24
14.89	0.48
33.10	0.86
62.52	1.24
155.22	1.68
523.39	2.62

Ferric Chloride,
(v=25.58 at 25° C.)

t	μ
25°	14.3
52	20.5
55	20.9
60	22.1
65	23.1
70	24.3
75	25.1
80	25.9
85	26.4
90	26.4
95	24.5
102	24.1
105	24.1
111	24.0
125	24.0

Mercuric Chloride,
$Hg\,Cl_2$.

v	μ
0.48	0.0031
1.15	0.0063
32.79	0.0490

SALICYLIC ALDEHYDE.

The sample of salicylic aldehyde from Schuchardt was rectified by redistillation. The portion taken had a constant boiling point and the specific conductivity was 5.98×10^{-6}.

TABLE VIII.

Solvent: salicylic aldehyde.

Ferric Chloride,[1]
$Fe\,Cl_3$.

v	μ
20.39	3.76
81.38	4.71
220.74	5.60

Ferric Chloride,
(v = 20.39 at 25° C.)

t	μ
25°	3.76
45	6.30
50	6.73
109	6.46

FURFUROL.

The sample of furfurol from Merck was treated with fused calcium chloride over which it stood for several weeks. It was then distilled and the distillate again distilled. The portion coming over between 156° and 158° at 744 mm. pressure was collected and its specific conductivity was 2.4×10^{-5}.

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[1] Apparently not quite all dissolved. After cooling became a very viscous mass.

TABLE IX.

Solvent: furfurol.

Ferric Chloride, $FeCl_3$. v	μ
45.60	20.78
80.98	22.20
149.21	26.42

Ferric Chloride, (v = 45.60 at 25° C.) t	μ
25°	20.78
45	37.83
55	40.98
65	44.06
75	47.96
85	51.41
95	56.07
105	60.02

ACETONE.

The acetone employed was treated with fused calcium chloride, over which it stood for several days and was then distilled. The distillate was again treated with calcium chloride and the distillate from this was redistilled twice and the portion having a boiling point at 56° C. at 744 mm. pressure was taken. The specific conductivity was less than 7.7×10^{-7}.

TABLE X.

Solvent: acetone.

Ferric Chloride, $FeCl_3$. v	μ
14.65	51.70
29.30	59.90
58.60	64.65
117.19	68.68
234.39	70.67
468.77	77.28
937.54	83.76
1,875.08	91.22

Antimony Trichloride, $SbCl_3$. v	μ
7.07	1.23
14.14	1.55
28.27	1.83
56.55	2.13
113.10	3.34

Stannous Chloride, $SnCl_2$. v	μ
37.78	8.77
75.56	8.09
113.33	6.87

Cupric Chloride, $CuCl_2$. v	μ
45.87	25.72
91.74	27.10
183.48	28.71
366.96	28.94
733.91	29.18

METHYL-PROPYL KETONE.

The sample of methyl-propyl ketone employed was from Schuchardt and gave a specific conductivity of 9.5×10^{-7}.

TABLE XI.

Solvent: methyl-propyl ketone.

Ferric Chloride, $FeCl_3$.		Ferric Chloride, ($v = 13.64$ at 25° C.)	
v	μ	t	μ
13.64	28.25	25°	28.25
22.83	31.07	49	33.47
53.36	36.98	50	33.66
100.71	42.76	55	33.79
111.13	41.59	60	34.07
164.43	46.15	70	35.60
358.09	50.28	75	35.89
1,074.27	59.52	80	36.17

$CuCl_2$ in less than 460.28 liters gave $\lambda = 5.22 \times 10^{-6}$. A resistance of 6000 ohms was introduced in the measuring.

ACETOPHENONE.

A sample of acetophenone from Schuchardt was treated with barium oxide, over which it stood for several days and then distilled. The distillate was redistilled and the portion coming over between 194° and 195° C. at 745 mm. pressure was taken. The specific conductivity of this portion was 1.8×10^{-7}.

TABLE XII.

Solvent: acetophenone.

Ferric Chloride, $FeCl_3$.		Ferric Chloride, ($v = 23.46$ at 25° C.)	
v	μ	t	μ
23.46	10.28	25°	10.28
46.71	11.03	50	15.17
65.77	11.59	65	17.52
124.91	12.03	80	20.52
292.98	13.08	100	23.90
		114	27.49
		125	28.74
		135	28.85
		150	28.16

ETHYL ACETATE.

The sample of ethyl acetate was treated several times with anhydrous copper sulphate, over which it stood for several days and then distilled each time. This last distillate was redistilled and the portion coming over between 76° and 77° C. at 738 mm. pressure was collected. The specific conductivity was 7.0×10^{-7}.

TABLE XIII.

Solvent: ethyl acetate.

Ferric Chloride,
$Fe\,Cl_3$.

v	μ
16.89	0.87
33.78	1.12
67.56	1.25

Antimony Trichloride,
$Sb\,Cl_3$.

v	μ
10.92	0.013
21.84	0.019

Stannous Chloride,
$Sn\,Cl_2$.

v	μ
68.05	0.042

Bismuth Trichloride,
$Bi\,Cl_3$.

v	μ
112.12	0.034

ETHYL MONOCHLORACETATE.

This solvent was a C. P. sample from Schuchardt, the boiling point of which was 143.5° C. The specific conductivity was less than 1.7×10^{-6}.

TABLE XIV.

Solvent: ethyl monochloracetate.

Ferric Chloride,
$Fe\,Cl_3$.

v	μ
7.76	12.45
14.96	13.14
19.18	13.49
22.09	13.75
45.63	14.78
92.05	16.38
152.55	17.88

Ferric Chloride,
($v = 7.76$ at 25° C.)

t	μ
25°	12.45
50	15.21
55	15.77
67	16.28
80	16.28
92	15.61
100	14.73
110	13.11

Antimony Trichloride,
$SbCl_3$.

v	μ
4.25	0.174
11.49	0.201
44.73	0.337

Cupric Chloride,
$CuCl_2$.

v	μ
13.32	1.24

Did not all dissolve;
so $\lambda = 1.33 \times 10^{-5}$.

ETHYL CYANACETATE.

This solvent was a C. P. sample from Schuchardt and was rectified by redistillation. The boiling point was very constant, and the portion collected came over between 203° and 203.5° C. at 744 mm. pressure. The specific conducting was 3.7×10^{-7}.

TABLE XV.

Solvent: ethyl cyanacetate.

Ferric Chloride,
$FeCl_3$.

v	μ
15.30	8.88
19.72	8.99
27.08	9.29
44.64	9.80
185.22	11.57

Silver Nitrate,
$AgNo_3$.

v	μ
10.62	4.19
19.00	4.78
28.30	5.29
58.57	6.46
110.97	7.66

Ferric Chloride,
($v = 15.30$ at 25° C.)

t	μ
25° C	8.88
49	13.40
60	15.85
75	20.14
87	22.44
100	24.83
125	29.49
150	38.70

Cupric Chloride.
$CuCl_2$.

v	μ
29.85	7.00
41.67	7.50
59.40	8.08
97.77	12.80

ETHYL ACETOACETATE.

The solvent employed was from Schuchardt, and was rectified be distillation. The portion which boiled between 174° and 176° C. at 736 mm. pressure was used. The specific conductivity was 4×10^{-7}.

TABLE XVI.

Solvent: ethyl acetoacetate.

Ferric Chloride,
$Fe\,Cl_3$.

v	μ
5.46	10.82
15.04	14.04
16.31	14.08
22.14	14.62
24.12	14.63
27.59	15.04
31.90	15.25
44.64	15.94
157.98	19.79
240.51	20.65
503.56	23.43

Antimony Trichloride,
$Sb\,Cl_3$.

v	μ
0.75	0.031
0.94	0.034
1.34	0.041
2.76	0.044
4.34	0.050
8.18	0.059
17.02	0.076
33.69	0.108
59.86	0.132
511.50	0.529

Mercuric Chloride,
$Hg\,Cl_2$.

v	μ
0.91	0.012
1.35	0.013
2.91	0.017
36.33	0.072

Phosphorus Trichloride,
$P\,Cl_3$.

v	μ
1.80	0.026
4.48	0.097

Stannic Chloride,
$SnCl_4$.

v	μ
2.02	1.08
4.13	1.71
8.76	2.37

Ferric Chloride,
(v = 5.46 at 25° C.
Solution two weeks old.)

t	μ
25° C	12.0
50	16.8
56	17.5
60	18.2
65	19.2
70	19.9
75	20.7
81	21.2
86	21.7
90	21.7
95	21.8
100	21.7

(Gases disengaged
at higher temperatures.)

Bismuth Trichloride,
$BiCl_3$.

v	μ
5.65	0.059
11.30	0.053
27.09	0.098
48.20	0.137
83.00	0.164
288.96	0.472

Arsenic Trichloride,
$As\,Cl_3$.

v	μ
0.47	0.087
0.65	0.071
0.84	0.068
1.13	0.067
1.37	0.067
2.49	0.084
3.60	0.070
10.20	0.085
31.13	0.114

ETHYL OXALATE.

This solvent was a C. P. sample from Merck, and its specific conductivity was 7.12×10^{-7}.

TABLE XVII.

Solvent: ethyl oxalate.

Ferric Chloride,
$Fe\,Cl_3$.

v	μ
13.15	5.88
22.07	5.89
42.29	5.92
94.79	6.25
342.85	7.70

Ferric Chloride,
($v = 13.15$ at 25° C.)

t	μ
25° C	5.88
50	8.11
62	9.21
75	10.15
100	11.14
125	9.58

(At 148° solution began to boil.)

ETHYL BENZOATE.

This solvent was a C. P. sample from Trommsdorff, and its specific conductivity was 1.8×10^{-7}.

TABLE XVIII.

Solvent: ethyl benzoate.

Ferric Chloride, $Fe Cl_3$.		Ferric Chloride, ($v = 29.54$ at 25° C.)	
v	μ	t	μ
29.54	1.55	25° C	1.55
174.28	1.61	56	1.16
517.21	1.91	75	0.82
		100	0.48

AMYL NITRITE.

This solvent was a C. P. sample from Schuchardt, and its specific conductivity was 1.8×10^{-7}.

TABLE XIX.

Solvent: amyl nitrite.

Ferric Chloride, $Fe Cl_3$.		Ferric Chloride, ($v = 21.34$ at 25° C.)	
v	μ	t	μ
21.34	1.54	25° C.	1.54
29.03	1.63	50	1.13
38.74	1.74	55	1.08
69.46	2.02	64	1.21
104.64	2.29	(At about 70° the solution began to boil.)	
264.16	3.00		
644.56	3.73		

NITROBENZENE.

The sample of nitrobenzene employed was from Kahlbaum and was prepared from crystallizable benzene. The specific conductivity was less than 3.5×10^{-7}.

TABLE XX.

Solvent: nitrobenzene.

Ferric Chloride,
$Fe\,Cl_3$.

v	μ
2.84	3.76
5.67	4.79
11.34	6.58
22.68	13.70
45.37	16.25
90.74	17.61
181.49	18.86
362.98	20.02
725.96	20.51
1,451.93	20.82
2,903.86	20.45

Ferric Chloride,
($v = 7.185$ at 25° C.)

t	μ
25° C	5.2
52	7.2
56	7.6
61	8.1
67	8.8
70	9.2
75	9.8
80	10.3
85	11.0
90	11.6
95	12.5
100	13.3
110	14.6
122	15.7
125	15.9
130	16.4
135	16.7
140	16.8
145	16.9
150	16.9

Phosphorus Trichloride,
$P\,Cl_3$.

v	μ
8.43	0.026
16.86	0.042

Antimony Trichloride,
$Sb\,Cl_3$.

v	μ
1.83	0.033
3.65	0.048
7.31	0.122
14.60	0.225
29.21	0.390
58.41	0.706
116.83	1.276

Bismuth Trichloride,
$Bi\,Cl_3$.

v	μ
8.50	0.80
17.01	0.91
34.02	0.96
68.04	1.03
136.07	1.07
272.14	1.11

Arsenic Trichloride,
$As\,Cl_3$.

v	μ
1.338	0.016
2.676	0.021
4.014	0.028

Aluminum Trichloride,
$Al\,Cl_3$.[1]

v	μ
4.692	3.67
9.384	4.51

---

[1] Dissolved with slight evolution of heat. When the dilutions were made the evolution of hydrochloric acid gas was very perceptible, and for this reason no further determinations were made. For the same reason the cryoscopic determinations do not appear among the results in Table XXI.

The following cryoscopic results will be of interest in connection with the conductivity measurements. The molecular weight determinations were made with a Bechmann's apparatus, and all of the usual precautions necessary to insure accurate results were observed. The solvent was the same as that employed in the conductivity measurements, but it was further purified by being recrystallized several times. The molecular lowering of the freezing point used in these calculations was 70.70 (see Ostwald's *Grundriss der allgemeinen Chemie*). The constant for nitrobenzene has been lately redetermined by Ampola and Carlinfanti[1] who give 69 as the new value, while from their calculation according to van't Hoff's formula they found it to be 68.6. The following results were not recalculated; for while the correction throughout would be the same and rather small, the relative values would remain practically the same.

TABLE XXI.

Solvent: nitrobenzene.

Ferric chloride, $Fe\,Cl_3$,

Mol. Wt. = 161.14.

Substance in 100 g solvent.	Lowering.	Mol. wt.
1.4792	0.330°	316.9
1.6510	0.433	269.6
1.9661	0.575	241.7
2.3582	0.728	229.2
3.0566	1.065	203.0
3.4823	1.255	196.2
4.0097	1.501	188.9
4.7389	1.756	190.8

Antimony Trichloride, $Sb\,Cl_3$,

Mol. Wt. = 225.06.

Substance in 100 g solvent.	Lowering.	Mol. wt.
2.5811	0.714°	255.6
3.1528	0.910	245.5
5.2983	1.585	236.3
6.3113	1.928	231.4
7.2706	2.248	228.7
8.3095	2.655	223.3
10.6533	3.555	211.9

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[1] Gazz, *Chem. Ital.*, **26**, II, 76; 1896. (Ref.) *Jour. Chem. Soc.*, **72** ii, 12; 1897.

Stannic Chloride, $Sn Cl_4$.

Mol. Wt. = 258.87

Substance in 100 g solvent.	Lowering.	Mol. wt.
2.1259	0.337°	445.9
3.4059	0.742	332.1
5.3896	1.242	306.8
6.8268	1.662	290.4

Arsenic Trichloride, $As Cl_3$,

Mol. Wt. = 179.98.

0.3997	0.223°	126.7
0.9756	0.493	139.9
1.2298	0.568	153.1
1.7010	0.763	157.6
2.7756	1.189	156.1
3.7299	1.554	169.7
4.5366	1.857	172.7
5.2582	2.138	174.3
6.4207	2.613	173.7
7.8651	3.179	174.9
10.4642	4.207	175.7

Bismuth Trichloride, $Bi Cl_3$.

Mol. Wt. = 312.08.

0.6833	0.230°	203.9
0.9190	0.250	258.1
1.1268	0.280	282.6
1.4927	0.340	301.8
1.8563	0.410	317.9
3.0829	0.662	326.9

Phosphorus Trichloride, PCl_3.

Mol. Wt. = 136.33.

0.9339	0.530°	124.6
1.3482	0.758	125.8

ORTHO NITROTOLUENE.

The C. P. sample of this solvent employed was from Kahlbaum, and the specific conductivity was less than 1.8×10^{-7}.

Table XXII.

Solvent: ortho nitrotoluene.

Ferric Chloride, $Fe\,Cl_3$.

v	μ
10.94	8.37
16.38	9.44
25.99	10.74
74.28	13.32
201.43	15.24

Ferric Chloride,[1] ($v = 10.94$ at 25° C.)

t	μ
25° C	9.39
46	11.98
60	12.77
70	12.92
80	12.67
90	12.12
100	11.46

Antimony Trichloride, $Sb\,Cl_3$.

v	μ
3.40	0.056
6.55	0.088
19.82	0.244
34.10	0.389

Murcuric Chloride, $Hg\,Cl_2$.

v	μ
105.43	0.628

META NITROTOLUENE.

The C. P. sample of this solvent was from Kahlbaum, and the specific conductivity was less than 1.8×10^{-7}.

Table XXIII.

Solvent: meta nitrotoluene.

Ferric Chloride, $Fe\,Cl_3$.

v	μ
10.86	6.86
46.93	11.10
84.77	12.55
448.14	19.00
814.81	18.20

Ferric Chloride, ($v = 10.86$ at 25° C.)

t	μ
25°	6.86
50	12.28
60	13.05
70	13.82
80	15.66
90	17.35
100	18.20
125	16.80

---

[1] This solution remained in the resistance cell for two hours before the determinations were made.

BENZONITRILE.

The C. P. sample of this solvent employed was from Trommsdorff, and the specific conductivity was 1.9×10^{-6}.

TABLE XXIV.

Solvent: benzonitrile.

Silver Nitrate, $AgNO_3$.		Silver Nitrate, ($v = 2.09$ at 25° C.)	
v	μ	t	μ
2.09	3.37	25° C.	5.55 (?)
9.43	5.18	50	6.75
16.33	6.37	56	7.05
24.06	7.66	65	7.59
44.62	10.12	77	8.11
58.98	11.19	87	8.75
83.92	13.41	95	9.26
151.96	16.38	105	9.65
301.21	18.20	114	10.09
803.24	21.64	125	10.69
		135	11.20
		150	11.70

PYRIDINE.

The sample of pyridine from König was fractionated, and the portion distilling over between 106° and 117° was treated with fused caustic potash from which it was distilled. The distillate was again treated with caustic potash, over which it stood for several days and was then distilled. The distillate was redistilled and the portion coming over between 113° and 114° at 742 mm. pressure was employed in some of the following determinations. The specific conductivity was 7.6×10^{-7}. For other determinations a C. P. sample of the solvent from Kahlbaum was employed and its specific conductivity was about 7.5×10^{-7}.

TABLE XXV.

Solvent: pyridene.

Ferric Chloride,
$FeCl_3$.

v	μ
6.06	7.96
15.02	7.52
24.56	6.85
42.18	6.82
95.35	6.41

Ferric Chloride,
$FeCl_3$.
(New series.)
(λ of solvent $= 1.74 \times 10^{-6}$)

v	μ
45.52	6.32
93.69	5.91
159.55	5.57

Ferric Chloride,
(v = 6.06 at 25° C.)

t	μ
25° C.	7.96
54	16.50
59	17.24
65	18.23
70	19.59
75	20.40
80	21.16
85	22.71
90	23.36
95	24.12
100	24.80
105	25.61
110	25.61

Silver Nitrate,
$AgNO_3$.

First series.

v	μ
7.55	24.07
10.71	24.87
17.70	25.79
25.52	26.91
27.43	27.29
37.32	27.96
51.43	29.49
60.90	30.17
93.71	30.83
140.57	36.21

Second series.

v	μ
392.28	40.16
588.42	43.13
784.56	45.21

Lead Nitrate,
$Pb(NO_3)_2$.

v	μ
21.10	0.81
55.96	1.57
168.47	3.25

Cupric Chloride,
$CuCl_2$.

v	μ
45.10	0.98
57.04	1.16

Mercuric cyanide,
$Hg(CN)_2$.

v	
5.35	0.012
13.09	0.014
357.42	0.153

Mercuric Iodide,
HgI_2.

v	μ
21.78	0.35
93.61	1.39
200.12	2.70

Silver cyanide,
Ag CN.

v	μ
14.64	4.78
24.52	5.04
38.40	5.42
100.47	6.16
393.01	6.47

Silver Tartrate,
$C_4 H_4 O_6 Ag_2$.

v	μ
340.74	14.64
1,505.91	35.29

Cobaltic Chloride,
$Co Cl_2$.

v	μ
74.06	0.20
805.31	1.45

A solution of cobaltic chloride becomes deep blue at a temperature between 40° and 50° C. The following specific conductivity determinations were made in order to ascertain whether the two differently colored solutions had the same conductivity.

	λ at 25°.	λ at 55°.
Solvent - - - - - - - -	7.5×10^{-7}	1.4×10^{-6}
Saturated solution of $Co Cl_2$ at 25° C. -	2.9×10^{-6}	5.5×10^{-6}

PIPERIDINE.

A C. P. sample of this solvent from Kahlbaum was employed, and its specific conductivity was less than 1.8×10^{-7}.

Table XXVI.

Solvent: piperidine.

Silver Nitrate,
$Ag NO_3$.

v	μ
4.24	0.368
5.25	0.277
7.88	0.154
10.50	0.091
15.62	0.043

Silver Nitrate,
(v = 4.24 at 25° C.)

v	μ
25°	0.368
30.5	0.391
35	0.432
40	0.453
45	0.478
50	0.508

QUINOLINE.

The sample of this solvent employed was from Merck, and its specific conductivity was 3.7×10^{-7}.

TABLE XXVII.

Solvent: quinoline.

Silver Nitrate, $AgNO_3$.		Silver Nitrate, ($v = 4.80$ at 25° C.).	
v	μ	t	μ
4.80	2.45	25° C.	2.45
9.60	2.79	50	4.67
34.92	2.80	62	5.20
129.83	3.62	70	5.52
		85	5.89
		104	5.75
		124	5.77
		136	5.52

GENERAL DISCUSSION OF RESULTS.

THE ALCOHOLS.

The non-aqueous solvents that yield solutions which conduct the best are in general the alcohols. Through the labors of Carrara,[1] Cattaneo,[2] Cohen,[3] Fitzpatrick,[4] Holland,[5] Kablukoff,[6] Pfeiffer,[7] Schall,[8] Schlamp,[9] Vollmer,[10] Zelinsky and Krapiwin,[11] and others, considerable knowledge concerning the conductivity of alcoholic solutions has been gained. Raoult,[1] Beckmann,[2] Woelfer,[3] Jones and King,[4] Salvadori,[5] and others from their boiling point determinations have likewise contributed a large number of facts that throw some light on the molecular condition of substances dissolved in alcoholic solutions.

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[1] (1) Gazz, *Chem. Ital.*, **24**, II, 504. (Ref.) *Jour. Chem. Soc.*, **68**, ii, 302; 1895. (2) Ibid., **26**, I, 119. (Ref.) *Jour. Chem. Soc.*, **70**, ii, 511; 1896. (3) Ibid., **27**, I, 422. (Ref.) *Jour. Chem. Soc.*, **72**, ii, 473; 1897.

[2] *Rend. Accad. Linc.*, II, 63 and 73; 1895. (Ref.) *Jour. Chem. Soc.*, **72**, ii, 537; 1897.

[3] *Zeit. phys. Chem.*, **25**, 1; 1898.

[4] *Phil. Mag.* (5), **24**, 322; 1887.

[5] *Wied. Ann.*, **50**, 261; 1893.

[6] *J. Russ. Chem. Soc.*, **28**, 391. (Ref.) *Jour. Chem. Soc.*, **64**, ii, 151; 1893.

[7] *Wied. Ann.*, **26**, 31; 1885.

[8] *Zeit. phys. Chem.*, **14**, 701; 1894.

[9] *Zeit. phys. Chem.*, **14**, 273; 1894.

[10] *Wied. Ann.*, **52**, 328; 1894.

[11] *Zeit. phys. Chem.*, **21**, 35; 1896.

Electrical conductivity determinations of many solutions of both organic and inorganic compounds in the following alcohols have been made: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, allyl, and benzyl. In most cases but few determinations have been made, and the conductivity is slight except in the case of the first three. In the methyl, ethyl, and propyl alcoholic solutions the value of μ approximates to, and in some cases exceeds, the value found in aqueous solutions; but in general it is much less. A few examples will illustrate this more fully. Lithium chloride in an aqueous solution gives a value of 95 for μ_∞ at 18° C.; while in propyl alcohol, in a volume of about 3,000 liters, the value of μ at 15° is given as 128.9. In fact, most of the values of μ in dilute solutions of propyl alcohol are, according to Schlamp, greater than the values of μ_∞ in water. In methyl alcohol the value of μ_∞ for $N(C_2H_5)_4I$ is 113.8, while in water it is only 104.2; for $S(C_2H_5)_3I$ μ_∞ is 112.5, while in water it is 107.6; in the case of $N(CH_3)_4I$ the values of μ_∞ in both solvents are virtually the same (115.3). According to the determinations in the other alcoholic solutions the values of μ do not even approximate those in aqueous solutions.

In order to calculate the degree of electrolytic dissociation of the dissolved substance, it is necessary to know the value of μ_∞. In non-aqueous solutions this value is more difficult to obtain, owing to the high resistance of the solutions employed. In alcoholic solutions these values have been usually obtained

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[1] *Compt. rend.*, **107**, 442; 1888; *Ann. de chim. et phys.*, **6**, 346; 1890

[2] *Zeit. phys. Chem.*, **6**, 437; 1890.

[3] *Wied. Ann.*, **57**, 91; 1896.

[4] *Am. Chem. Jour.*, **19**, 753; 1897.

[5] Gazz. *Chem. Ital.*, **26**, I, 237; 1896. (Ref.) *Jour. Chem. Soc.*, **70**, ii, 712; 1896.

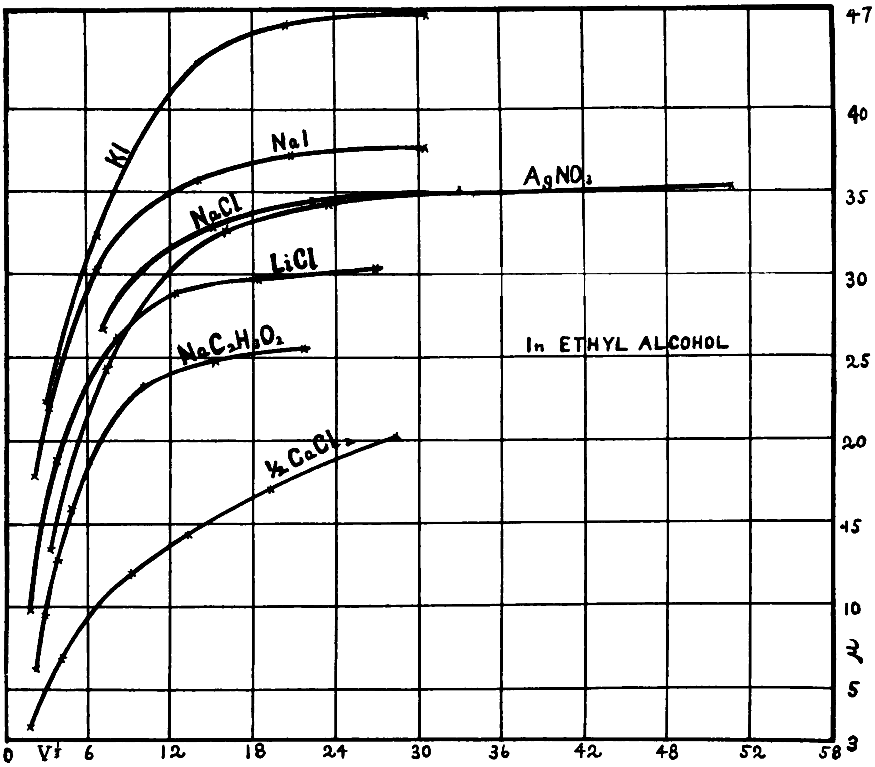
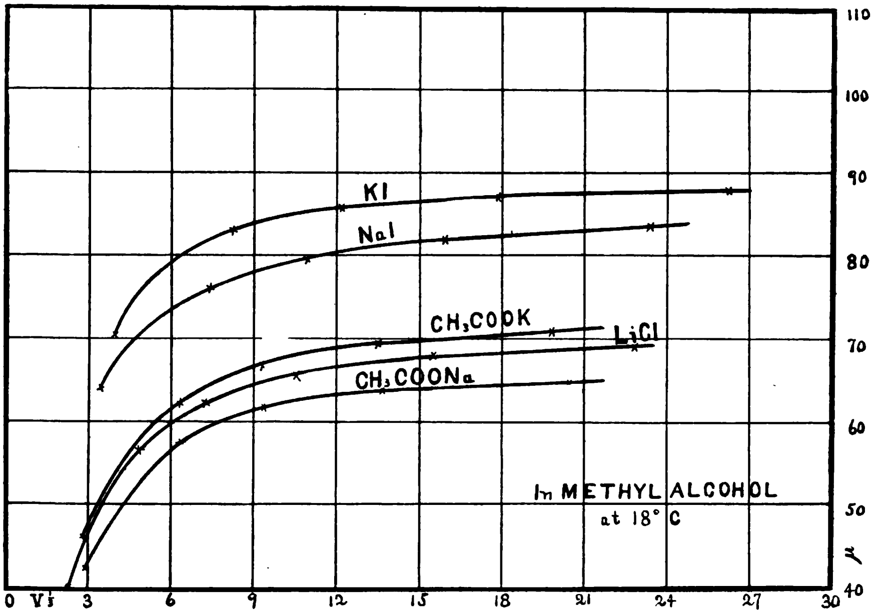
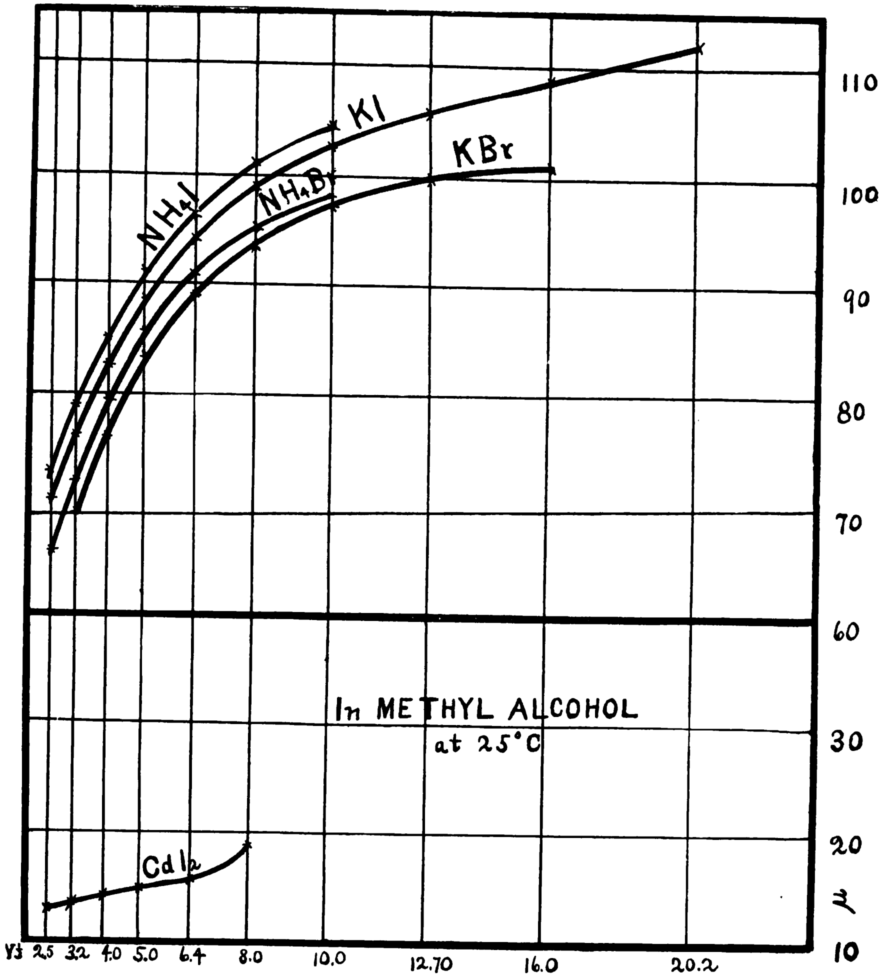

KI
NaI
NaCl
AgNO3
LiCl
NaC2H3O2
½ CaCl2
In ETHYL ALCOHOL
47
40
35
30
25
20
15
10
λ
5
3
0
V⅓
6
12
18
24
30
36
42
48
52
58

Plate III.


KI
NaI
CH_3COOK
LiCl
CH_3COONa
In METHYL ALCOHOL
at 18° C
0
V⅓
3
6
9
12
15
18
21
24
27
30
110
100
90
80
70
60
50
μ
40


KI
KBr
NH4I
NH4Br
CdI2
In METHYL ALCOHOL
at 25°C
110
100
90
80
70
60
30
20
15
10
V3 2.5
3.2
4.0
5.0
6.4
8.0
10.0
12.70
16.0
20.2

by experiment, while in other cases they have been extrapolated. This will subsequently be shown to be unjustifiable.

In Plate II is platted the molecular conductivity of various salts in ethyl alcoholic solutions, from the determinations of Vollmer at 18°. The molecular conductivity is represented by ordinates, and the cube root of the volume, in which one gram-molecule of the substance was dissolved, is represented by abscissas. The cube root of the volumes was employed in order to represent the values for the more dilute solutions in the figure.

It will be noticed that the salts of the alkalies yield limiting values for μ, while in the case of $CaCl_2$ there seems to be no tendency for the curve to become asymptotic. The same is true for $Ca(No_3)_2$, and from my determinations for $FeCl_3$ and $SbCl_3$.

In Plate III is represented the molecular conductivity of salts in methyl alcohol from Vollmer's determinations at 18° C. and in Plate IV the results of Zelinsky and Krapiwin determined at 25° C.

In most cases it will be seen limiting values are reached, CdI_2 being, however, an exception. Zelinsky and Krapiwin's determination for KI indicates that the curve would not become asymptotic, and therefore no limiting value for μ would be reached. Nevertheless, Carrara assigns 97 as the value of μ_∞, and Cohen[1] has pointed out that the difference in the determinations of Carrara and of Zelinsky and Krapiwin may be attributed to the effect of the platinum black electrodes, which they used, on the alcohol.

Carrara calculated the values of μ_∞ for a number of salts in methylic alcohol solutions and found them to agree very closely with his own experimental results. In the following table are given these results and also the value of μ_∞ in water.

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[1] Loc. cit.

TABLE XXVIII.

Values of μ_∞.

	IN METHYL ALCOHOL.				IN WATER.			
	Cl	Br	I	OH	Cl	Br	I	OH
H	133.80	....	134.5	....	395.2	398.	397.	....
Li	77.30	....	....	....	110.0	....	....	....
Na	86.80	87.58	89.77	71.83	119.4	122.2	121.4	216.2
K	95.57	96.52	97.63	75.75	140.8	143.6	142.6	237.6
NH_4	96.24	99.93	105.25	(82.0)	140.6	143.4	142.6	230.0
$N(CH_3)_4$	....	....	115.30	....	....	....	115.6	....
$N(C_2H_5)_4$	95.76	96.62	113.76	91.13	102.4	105.2	104.2	199.2
$S(CH_3)_3$	100.09	102.5	116.38	97.34	117.8	120.3	119.3	214.0

Carrara's calculations of μ_∞ were based upon Campetti's[1] determinations of the transference figures of the halogens in methylic alcohol solutions. From these values Carrara also calculated the rate of migration of the ions and the results are given in the following table which is taken from the *Jahrbuch der Electrochemie* **3**, 13, 1896:

TABLE XXIX.

Speed of Migration.

	IN METHYL ALCOHOL.			IN WATER.
	Cl	Br	I	
Li	27.83	.....	.....	39.8
Na	37.33	37.33	37.33	49.2
K	46.10	46.26	45.19	70.6
NH_4	46.77	49.49	53.81	70.4
$N(CH_3)_4$	.....	.....	63.08	43.6
$N(C_2H_5)_4$	46.29	46.36	61.34	32.2
$S(CH_3)_3$	51.43	49.85	63.94	47.6
H	85.53	.....	82.50	325.0
OH	32.00			170.0
Cl	49.47			70.2
Br	50.24			73.0
I	52.44			72.0
CH_3COO	32.99			38.4
CCl_3COO	35.95			32.8

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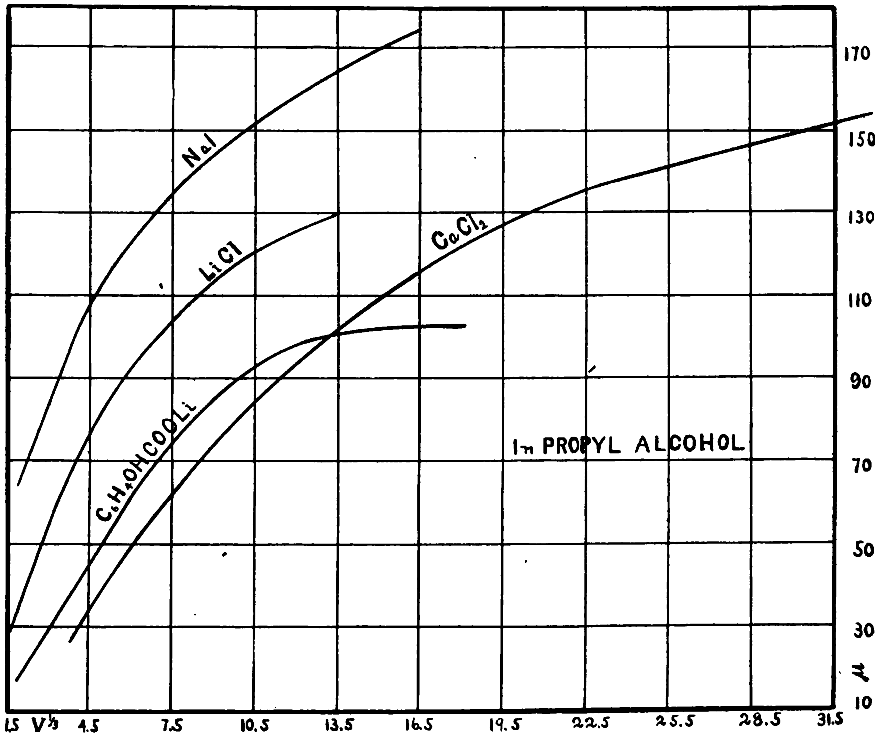
[1] *Nuovo Cimento* [3] **35**, 225; (Ref.) *Jahr. der Electrochemie*, **1**, 22; 1894.


NaI
LiCl
CaCl₂
C₆H₄OHCOOLi
1n PROPYL ALCOHOL
170
150
130
110
90
70
50
30
μ
10
1.5 V⅓
4.5
7.5
10.5
13.5
16.5
19.5
22.5
25.5
28.5
31.5

Kawalki[1] found that the diffusion coefficient of a number of substances in ethyl alcohol is 0.34 times as great as in water. Vollmer[2] from his work observed that the conductivity in ethyl alcoholic solutions at 18° C. is approximately 0.34 times as great as in aqueous solutions, while his empirical factor for methyl alcohol is 0.73. In general, then, limiting values can be obtained for μ in methyl and ethyl alcoholic solutions.

In other alcoholic solutions no such uniformity seems to exist. This is perhaps best illustrated in the case of solutions in propyl alcohol. The molecular conductivity of solutions in this solvent are represented in Plate V. The determinations are from Schlamp's[3] work with this solvent.

It will be noted that lithium salicylate is the only salt the conductivity of which appears to approach a limiting value. Schlamp does not hesitate, however, to assign values for μ_∞ in all cases and from the platted results this seems hardly justifiable.

The conductivity has been found to increase with the temperature. In my determinations with both allyl alcohol and benzyl alcohol this was also found to be the case. (See quantitative results—Tables IV and V.)

Raoult found that the vapor pressure of alcohols is very slightly lowered by the addition of the dissolved substance. The subject has been further investigated by Woelfer, who finds a considerable rise in the boiling point of methyl and ethyl alcohol when various substances are added. The calculated values are usually lower than the theoretical values for the molecular weights of the dissolved substances. In methylic alcohol solutions the degrees of dissociation as calculated from the boiling point determinations, show closer agreement with those obtained by the conductivity method than in the case of the other alcoholic solutions. In the following table from Woelfer are given the values of the degree of dissociation, α, as calculated from the boiling point determinations of Woelfer and the conductivity measurements of Vollmer.

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[1] *Wied. Ann.*, **52**, 300; 1894.

[2] Ibid., **52**, 328; 1894.

[3] *Zeit. phys. Chem.*, **14**, 272; 1894.

TABLE XXX.

Values of α.

Salt.	Per cent.	From boiling point.	From conductivity.
LiCl	0.45	0.63	0.57
KI	0.36	0.61	0.79
NaI	0.44	0.87	0.74
$CH_3COO\ K$	0.48	0.48	0.63
CH_3COONa	0.40	0.49	0.63

Salvadori[1] found $HgCl_2$ to be more highly dissociated in methyl alcohol according to the boiling point method than in aqueous solutions. Beckmann[2] found the reverse to be true in ethyl alcoholic solutions. Jones and King[3] calculated the dissociation of KI from their boiling point determinations, to be 25.4 per cent. in a 2 per cent. solution and 27.2 per cent. in a 3 per cent. solution of ethyl alcohol, i. e., the dissociation increases with the concentration. Cohen,[4] from conductivity determinations at 18° C., found the degree of dissociation to increase with the dilution, the dissociation being about 80 per cent. at a dilution of about 1000 liters. This disagreement of the dissociation values obtained by these two methods will be made more apparent, perhaps, by Table XXXI. The table is copied from Woelfer's paper. The results by the boiling point method were obtained by himself, those by the conductivity method by Vollmer.

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[1], [2], [3], [4] Loc. cit.

TABLE XXXI.

Values of α.

Salt.	Per cent. in ethyl alcohol.	From boiling point.	From conductivity.
LiCl	0.9	0.35	0.32
CH_3COOK	1.07	0.18	0.27
KI	0.78	0.29	0.49
$AgNO_3$	0.533	0.65	0.38
NaI	2.14	0.27	0.45
NaI	0.68	0.51	0.56
CH_3COONa	0.97	0.01	0.24

It is to be remembered that these two sets of values are calculated from results obtained at different temperatures; in the case of the conductivity measurements at 18° C., where the viscosity factor is about 0.01211, and in the other case at 78° when that factor had decreased (at 70° to 0.00521). Yet it will be seen that there is no regularity of the results and that the degree of dissociation according to the boiling point determinations is not invariably higher than that obtained by the conductivity method. It is no doubt but proper to ask, which of these methods gives the correct measure of the amount of dissociation of the dissolved substance.

In propyl alcoholic solutions the boiling point method gives nearly normal values for the molecular weights of the dissolved substances. In the case of lithium salicylate, however, a double molecular is indicated; and it is only in the case of solutions of this salt, that the values for μ appear to approach a limiting value. (See Plate V.) The results of a few of the molecular weight determinations made by Schlamp are given in the following tables:

TABLE XXXII.

Salicylate of Lithium.		Sodium Iodide.		Lithium Chloride.	
Mol. Wt. = 144.		Mol. Wt. = 150.		Mol. Wt. = 42.5.	
Per cent. Content.	Mol. Wt.	Per cent. Content.	Mol. Wt.	Per cent. Content.	Mol. Wt.
1.97	260	3.09	144.8	0.182	36.19
2.16	273.3	5.09	146.1	4.05	48.95
4.86	252.5	7.60	140.1	4.57	45.40
10.30	273.4	14.02	150.5	5.0	42.3
15.45	288.9				

From the analogy of the electrolytic dissociation of substances in aqueous solutions to the dissociation of gases, Ostwald has formulated a law of dilution for binary electrolytes which is as follows:—

$$K = \frac{\alpha^2}{(1-\alpha)V}; \qquad \alpha = \frac{\mu_v}{\mu_\infty}$$

and V is the volume in which one gram molecule of the dissolved substance is contained. In aqueous solutions of weak electrolytes this generally holds fairly well, and many attempts have been made to determine whether it holds for non-aqueous solutions. Most investigators, Vollmer, Woelfer, Cattaneo, and others, have found that Ostwald's dilution law does not hold in the case of methyl and ethyl alcoholic solutions. Cohen[1] has considered this subject at considerable length, and comes to the same conclusion.

The following table compiled from the work of Vollmer and of Woelfer shows more clearly in the case of ethyl alcoholic solutions that the K in the above formula is not constant.

TABLE XXXIII.

From Vollmer's conductivity determinations.

Potassium Acetate.			Lithium Chloride.			Sodium Iodide.		
v	α	100K	v	α	100K	v	α	100K
11.4	0.264	0.83	5.9	0.328	2.70	8.7	0.474	4.92
113.0	0.549	0.59	60.5	0.621	1.68	27.4	0.580	2.92
1120.0	0.862	0.48	605.0	0.858	0.86	280.	0.805	1.19
3520.0	0.934	0.36	1912.0	0.934	0.69	2800.	0.934	0.47

From Woelfer's boiling point determinations.

Potassium Acetate.			Lithium Chloride.			Sodium Iodide.		
v	α	100K	v	α	100K	v	α	100K
6 0	0.077	0.11	2.6	0.178	1.5	9.1	0.289	1.3
6.9	0.100	0.16	3.0	0.205	1.8	10.4	0.317	1.4
8.0	0.126	0.22	3.5	0.240	2.2	12.2	0.353	1.6
9.7	0.160	0.31	4.2	0.277	2.5	14.7	0.391	1.7
12.2	0.195	0.39	5.3	0.325	2.9	18.4	0.438	1.8
16.2	0.249	0.50	7.0	0.381	3.4	24.6	0.495	1.9
24.4	0.324	0.64	10.6	0.472	4.0	37.0	0.574	2.1
48.4	0.441	0.71	21.1	0.600	4.3	74.0	0.718	2.4

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[1] Loc. cit.

Rudolphi's formula, which differs from Ostwald's in having $\sqrt{V}$ for V, has been shown to hold no better than Ostwald's. The values of the constant as calculated by these two formulæ from the conductivity determination of potassium acetate, are given in the following table for comparison. K with the subscript r indicates that those values were obtained by using Rudolphi's formula, while K with the subscript o indicates that Ostwald's formula was employed.

TABLE XXXIV.

v	μ	100 K_r	100 K_o
11.4	8.28	0.82	0.242
113	17.18	0.59	0.055
1,120	27.0	0.49	0.014
3,520	29.2	0.36	0.006

It will be observed that Rudolphi's formula does not yield a constant.

From the preceding it therefore appears that neither the dilution law of Ostwald nor that of Rudolphi holds for alcoholic solutions.

It has been shown from Schlamp's work that the assumption of values for μ_∞ is not justified; therefore, since these values are wanting, the validity of the law of Ostwald and of that of Rudolphi cannot be tested in regard to this solvent. The data available are not sufficient to draw any conclusions concerning the applicability of these laws of dilution to other alcoholic solutions.

Nernst[1] has called attention to the fact that solvents which have a high dielectric constant yield solutions that conduct electricity. This is true in the case of alcoholic solutions, but those solvents that have the highest dielectric constant do not always yield solutions that conduct the best; but in general this is the case. Propyl alcohol, the dielectric constant of which is only about four-fifths that of ethyl alcohol, generally yields solutions that conduct better; the reverse is the case, however, when hydrochloric acid is the dissolved substance. Further, methyl alcohol, the dielectric constant of which is about 32, yields dilute solutions of $S(C_2H_5)_3I$ that conduct better than those in water, the dielectric constant of which is about 80. The reverse is the case in concentrated solutions. (See Table XXVIII.)

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[1] *Zeit. phys. Chem.*, **14**, 622; 1894.

The coefficients of association of the alcohols show that their molecules are polymerized, but the conductivity is not proportional to the degree of polymerization. The illustrations given above in regard to the dielectric constants are applicable here as well.

The conductivity increases with the temperature for the determinations that have been made, and no exception has as yet been found. There are not sufficient data to determine accurately the temperature coefficient of all alcoholic solutions; but it can be stated that, in general, the conductivity does not increase proportionately with the temperature. It has been pointed out by Holland and by Zelinsky and Krapiwin — and later it has been confirmed by Cohen as well as by Walker and Humbly[1] — that the temperature coefficient seems to be but slightly influenced by the addition of a non-electrolyte or even of a small quantity of water.

The investigation that has been carried on with mixtures of water and alcohol is of considerable magnitude; but as it has very little bearing upon the subject in hand, not much attention has been paid to it, and consequently very little reference will be found to it in this discussion. But it might be within the compass of this work to mention the investigations of Cohen[2] and perhaps those of Zelinsky and Krapiwin.[3] The following table of comparative conductivities is taken from the work of Zelinsky and Krapiwin. In the column headed A is given the conductivity in aqueous solutions, under B in methyl alcoholic solutions, and under C is given the conductivity in a 50 per cent. solution of methyl alcohol and water.

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[1] *Jour. Chem. Soc.*, 71, i, 66; 1897.

[2], [3] Loc. cit.

Table XXXV.

V	KBr			NH_4Br			KI			NH_4I		
	A	B	C	A	B	C	A	B	C	A	B	C
16	123.1		59.82	127.2	65.43	61.16	124.5	69.20	62.13	125.4	72.24	62.63
32	127.5	69.02	62.46	131.8	72.73	63.81	128.2	76.35	64.37	129.6	78.74	65.04
64	130.5	76.70	65.36	135.3	79.56	66.04	130.5	82.52	66.01	133.4	85.0	67.48
128	132.9	83.60	67.11	138.6	85.80	67.45	133.0	88.69	67.45	135.9	91.14	69.28
256	136.4	88.96	69.26	141.2	90.88	68.32	135.8	93.85	68.28	138.7	96.20	70.34
512	140.2	93.26	70.53	143.5	94.99	69.10	137.9	98.19	69.65	141.3	100.6	71.12
1024	143.4	97.25		145.6	98.24	70.11	140.9	102.2	70.55	143.7	104.7	71.57

It will be noticed that the conductivity of the halogen salts of the alkalies in methyl alcohol (B) is considerably less than in aqueous solutions (A). When water is added to the extent of 50 per cent. even (C), the conductivity is somewhat less than it is in absolute methyl alcohol. Cohen and others have pointed out the same fact; that is, at 18° C. the conductivity of a mixture consisting of water and methyl alcohol, and containing more than 60 per. cent of alcohol, is less in dilute solutions than it is in absolute alcohol. This fact seems to be rather difficult to reconcile with the electrolytic dissociation theory, for here we have two solvents that possess dissociative power in a high degree, and yet a salt dissolved in a mixture of equal parts of these yields a solution the conductivity of which is less than that of the solutions formed when dissolved in either.

Carrara[1] has shown that the electrolytic dissociation of water in methyl alcohol is greater than it is in aqueous solutions, while the reverse is the case in ethyl alcohol. It is also of interest to note that KOH and NaOH in methyl alcohol show the same conductivity as CH_3OK and CH_3ONa.

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[1] Gazz., *Chem. Ital.*, **27**, I, 422; 1897. (Ref.) *Jour. Chem. Soc.*, **72**, ii, 473; 1897.

THE ALDEHYDES.

From the quantitative measurements of the electrical conductivity of solutions in aldehydes, the results of which are given in Tables VI, VII, VIII and IX, it will be observed that furfurol yields the largest values of μ for solutions of ferric chloride. The dielectric constant of this solvent is larger than that of any of the other aldehydes. Owing to the great volatility of acetic aldehyde, satisfactory quantitative measurements at 18° C. were not made; but from the qualitative results it will be seen that this solvent yields solutions that conduct fairly well.

The magnitude of the molecular conductivity can be readily seen from the results. The value of μ increases with the dilution in all cases except for the solution of ferric chloride in benzaldehyde. The conductivity increases with the temperature, except in the case of the solution of the trichloride of antimony in paraldehyde, in which instance the conductivity appears to remain virtually constant. In the solution of ferric chloride in salicylic aldehyde the conductivity becomes practically constant at about 45° C.

The coefficents of association of the aldehydes, as far as these could be found in the literature of the subject, indicate that their molecules are not polymerized.

THE KETONES.

The ketones were found to yield solutions that conduct electricity fairly well. Considerable work has been done with these solvents. The conductivity of the solutions of a number of salts, both organic and inorganic, has been measured by Laszczynski,[1] Carrara,[2] Dutoit and Aston[3] and some boiling point determinations in acetone have been made by Dutoit and Friderich.[4]

Acetone yields solutions the conductivity of which is in gen-

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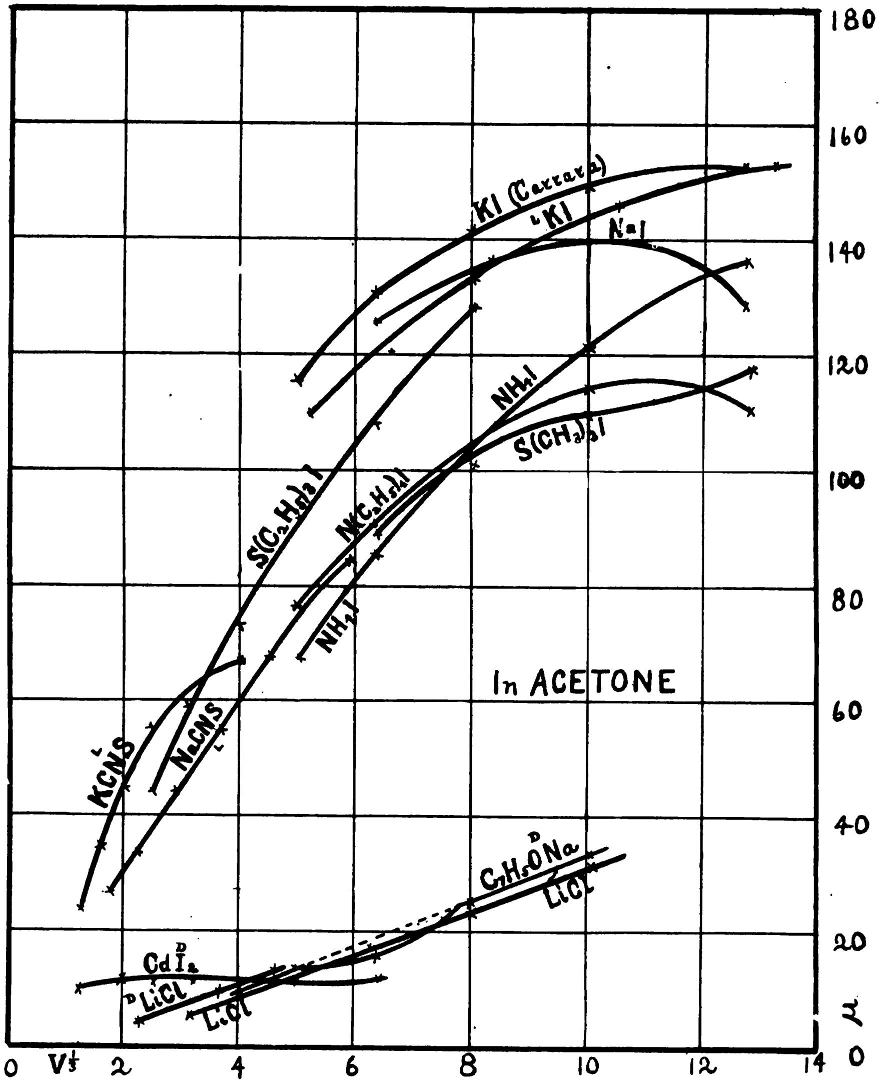
[1] *Zeit, Electrochemie*, **2**, 55; 1895.

[2] Gazz, *Chem. Ital.*, **27**, I, 207; (Ref.) *Jahr. der Electrochemie*, **4**, 48; 1897.

[3] *Comptes rendus*, **125**, 240; 1897.

[4] *Bull. Soc. Chim. Paris* (3) **19**, 321; 1898.


KI (Carrara)
L KI
NaI
NH4I
S(CH3)3I
S(C2H5)3I
N(C2H5)4I
NH4I
L KCNS
NaCNS L
In ACETONE
D C7H5ONa
LiCl
D CdI2
D LiCl
LiCl
0 V⅓ 2 4 6 8 10 12 14
180 160 140 120 100 80 60 40 20 λ 0

eral better than in the case of many of the other ketones; and on Plate VI is represented the conductivity of a number of salts in this solvent. The results platted are from the determinations of Carrara principally, those designated L from Laszczynski, and those with D are from Dutoit and Aston.

It will be observed, that the molecular conductivity of the solutions of all the salts increases with the dilution except that of cadmium iodide, which remains virtually constant. Dutoit and Friderich found the same to be true for cadmium iodide in acetophenone. In the case of solutions of this salt in both methyl-ethyl ketone and methyl-propyl ketone, the conductivity decreases with the dilution and the same was found to be the case for stannous chloride in acetone. (See Table X.)

In general the conductivity of solutions in ketones is much less than that of aqueous solutions, but there are a few noticeable exceptions. The molecular conductivity of NaI, NH_4I, $N(C_2H_5)_4I$ and of $S(C_2H_5)_3I$ in acetone, according to Carrara, is greater in dilute solutions than the values assigned μ_∞ for aqueous solutions. The value of μ for most of these salts is greater in acetone than in methyl alcohol. Carrara finds that HCl, LiCl and other hygroscopic substances that are highly dissociated in water, yield very low values for the molecular conductivity when dissolved in ketones. The value of μ for $SCN.NH_4$, CdI_2, and $C_7H_5O_2.Na$ in methyl-propyl ketone as well as those for most salts in acetophenone are not of great magnitude.

It will be seen from Plate VI that very few of the salts yield solutions in acetone that have limiting values for μ. There are two curves, for NaI and $N(C_2H_5)_4I$, that appear to indicate a decrease in the conductivity after certain dilutions are reached. The two curves, platted for KI, one from the determinations of Laszczynski and the other from those of Carrara, apparently intersect at about $\mu = 153$. Laszczynski thinks the value of μ_∞ lies between 160 and 170. Assuming the value of 160 for μ_∞, according to Kohlrausch's law of the additive property of the conductivity of aqueous solutions, Laszczynski calculates the factor k in the formula, $\mu_\infty = k\,(u + v)$, where $(u + v)$ is the conductivity at infinite dilution in water and k is a constant. The value of k he finds to be 1.3 for acetone. If this method be applied to salts other than KI, the one he employed—to CdI_2 for instance—, it will be found that new values for k will be obtained. There is no such agreement between the limiting values of μ in acetone and water as Vollmer found to hold in the case of ethyl alcohol and water. The two curves for LiCl are alike; but the values of μ differ slightly, neither, however, showing any tendency to approach a limiting value. The small conductivity Carrara[1] ascribes to the combination of salt and solvent which forms $LiCl + C_3H_6O$.

There have been too few molecular weight determinations of salts in ketones made by the boiling point method. This method, according to Dutoit and Friderich,[2] yields normal molecular weights for the compounds of the formula $CNS.NH_4$, $HgCl_2$, NaI, LiCl, and CdI_2 when dissolved in acetone. In conjunction with the electrical conductivity of these solvents, this seems to argue against the electrolytic dissociation theory, if the methods employed are trustworthy means for measuring the amount of dissociation in non-aqueous solutions. But Dutoit and Friderich expect soon to show that this is not incompatible with the dissociation theory.

From the magnitude of the dielectric constants, one would expect the ketones to yield solutions that conduct. According to Ramsay and Shields, their molecules are polymerized. As far as measurements have been made, the conductivity has been found to increase with the temperature, except in the case of CdI_2 where it remained the same at 50° C as at 25°; but it must also be remembered that the molecular conductivity of solutions of this salt does not change with the dilution.

THE ESTERS.

In esters the dissociative power is slight, and decreases with an increase in the carbon content. The substitution of Cl, CN or CH_3CO for the hydrogen of the methyl group does not cause a decrease in the dissociative power of the solvent. Ethyl carbonate does not conduct, but if one of the ethoxy groups be replaced by Cl, the resulting compound possesses dissociative power to a considerable degree. Ethyl monochloracetate yields solutions that conduct fairly well, while the substitution of the CN group, (thus forming ethyl cyanacetate) yields solutions of ferric chloride that do not conduct as well as those of ethyl monochloracetate; but the reverse is true in the case of solutions of $CuCl_2$. By comparison of Tables XIV, XV, and XVI, it will be seen that neither of these solvents yields solutions that conduct as well as the solutions of ethyl acetoacetate, as far as examined. The esters with the highest dielectric constants usually yield solutions that conduct the best, but there are a few exceptions to this. From Tables XVI and XV it will be seen that ethyl acetoacetate yields solutions of ferric chloride that conduct better than those in ethyl cyanacetate, the dielectric constant of the latter being 26.7, while that of the former solvent is only 15.7. Then, too, those esters whose dielectric constants are very low yield solutions that conduct electricity slightly—for example, ethyl acetate and ethyl benzoate.

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[1] Loc. cit.

[2] Loc. cit.

The coefficients of association that have been determined, show that the molecules of these esters are not polymerized; yet it will be noted that ethyl acetoacetate yields solutions that conduct very well. In all determinations made, it was observed that the conductivity increases with both the dilution and the temperature.

COMPOUNDS CONTAINING NITROGEN.

The nitro compounds of benzene and toluene yield solutions that conduct fairly well. The conductivity increases with the dilution, and in the ferric chloride solution μ approaches a limiting value. The conductivity of other salts in nitrobenzene is rather low. (See Table XX.) The results of a number of cryoscopic determinations are given in Table XXI. From these it will be observed that the values obtained seem to indicate normal molecular weights for the dissolved substances. These determinations indicate that the molecular weight of ferric chloride is uniformly higher than the theoretical, and decreases with increased concentration of the solution. The same is true in the case of the trichloride of antimony, but the variation is relatively less than in the case of the ferric chloride; and the more concentrated solutions show a molecular weight slightly less than the theoretical. In the case of stannic chloride the same general facts appear. The trichlorides of bismuth and phosphorus yield molecular weights that increase with the concentration. In the more dilute solutions these values are lower than the theoretical. These results are of particular interest in connection with the high values of μ obtained in this solvent for solutions of ferric chloride. The conductivity is in keeping with the high dielectric constant of nitrobenzene; and according to Ramsay and Shields this solvent is classified among those whose molecules are not polymerized. The conductivity increases with the temperature, and reaches a limiting value. (See Table XX.)

Dutoit and Aston have determined the conductivity of a number of salts in propionitrile. The conductivity of various salts in solutions of acetonitrile and butyronitrile has been measured by Dutoit and Friderich. They find that nitriles yield solutions that conduct, and the same is true of benzonitrile. (See Table XXIV.) Owing to the small quantity of this solvent available, only a few quantitative determinations could be made; but from the qualitative results it will be seen that benzonitrile solutions conduct fairly well. The values of μ for acetonitrile solutions approximate closely those obtained for aqueous solutions, while for $CNS.NH_4$ and NaI, μ is about the same magnitude as for $AgNO_3$ in benzonitrile. The conductivity of the other salts in these solvents is rather low. The conductivity increases with the dilution, but in the case of NaI in butyronitrile it appears to be about constant. The conductivity increases with the temperature except in the case of solutions of CdI_2 in acetonitrile, the value of μ being virtually the same at 0.2° C. as at 37.2° C.

According to Werner,[1] boiling point determinations indicate normal molecular weights of $AgNO_3$ in benzonitrile. The average of his determinations is 176, while the theory requires 170. His values for mercuric iodide are a little above the

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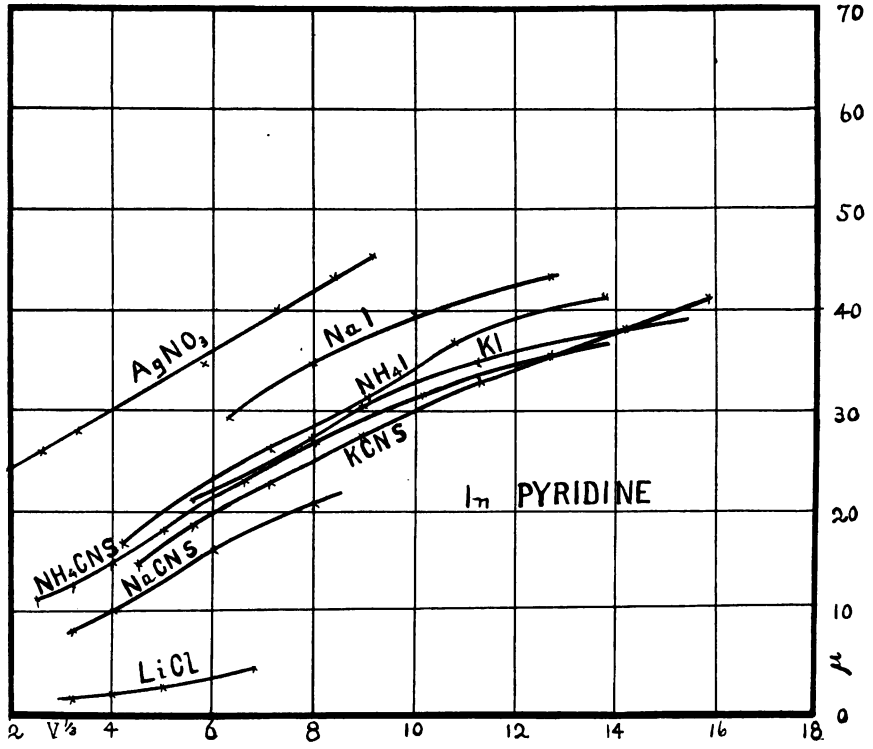
[1] *Zeit. Anorg. Chem.*, **15**, 1; 1897.

Plate VII.


AgNO₃
NaI
NH₄I
KI
NH₄CNS
NaCNS
KCNS
LiCl
In PYRIDINE
70
60
50
40
30
20
10
μ
0
2
V⅓
4
6
8
10
12
14
16
18

normal, while the average of two series shows normal values for $HgCl_2$. The qualitative results given above show that solutions of $HgCl_2$ conduct electricity.

The coefficients of association of the nitriles show that their molecules are polymerized, with the exception of benzonitrile. This solvent shows a high value for its dielectric constant; but no values for the other nitriles could be found in the literature.

ORGANIC BASES.

Of the organic bases investigated, pyridine and quinoline were found to yield solutions that conduct electricity much better than piperidine. Laszczynski and Gorski[1] have determined the conductivity of a number of salts in pyridine, and their results are platted on Plate VII.

Lithium chloride, it will be noticed, yields solutions that conduct very poorly; and the authors attribute this fact, as Carrara did in the case of this salt in acetone, to the combination of the solvent with the dissolved substance forming $LiCl + 2\,C_5H_5N$. They assign limiting values to μ in the case of $NH_4.CNS$, NH_4I, KI and NaI. From Plate VII it appears that the curves representing the conductivity would become asymptotic. The values for $AgNO_3$ are my own determinations, and these do not appear to approximate a limiting value for μ at least in the dilutions at which the measurements were made. A glance at Table XXV will show that the silver salts give larger values for μ than even the salts of the alkalies, according to Laszczynski and Gorski.

Werner's[2] boiling point determinations show about normal molecular weights for the salts of the heavy metals in pyridine. The average of his determinations for $AgNO_3$ is 165.4, — theory 169.55; for $Hg(CN)_2$, 216.68, — theory 251.76; for HgI_2, 308.0, — theory 452.88; and for $Pb(NO_3)_2$, 352.07, — theory requires 330.35. In most cases he obtained values a little under the theoretical. The greatest discrepancy occurs in the case of HgI_2, and it will be observed that the solution of this salt yields small values for μ.

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[1] *Zeit, Electrochemie*, **4**, 290; 1897.

[2] Loc. cit.

The dielectric constants of these solvents have not been determined to my knowledge. The coefficients of association of pyridine and quinoline do not indicate polymerization of their molecules, while that of piperidine indicates a slight polymerization. It will also be noted that this last named solvent yields solutions that conduct very much more poorly than either of the others. Werner's molecular weight determinations in piperidine give values somewhat higher than the theoretical: for example, the average of three determinations for $AgNO_3$ is 188.88 whereas the theory requires 169.55.

THEORETICAL PART.

Through the efforts of various investigators of non-aqueous solutions, a large number of facts have been accumulated which have been rather difficult to explain satisfactorily by means of the generally accepted theory of electrolytic dissociation. From time to time additional theories have been promulgated to explain these facts; until, at the present time, many have been advanced by means of which explanations have been attempted and from which generalizations have been drawn — in some cases apparently without sufficient experimental data to warrant them. A brief survey of the explanations offered will now be given, and an effort will be made to show wherein these are not reconcilable with the experimental results herein presented.

From a consideration of the optical properties of solvents, Brühl[1] comes to the conclusion that oxygen is generally tetravalent. He attributes the polymerization of the molecules of water and of other oxygenated liquids, their high specific inductive capacity, as well as the dissociative power exerted upon the dissolved substance, to their being unsaturated compounds. It is true that a great many oxygenated solvents do yield solutions that conduct electricity; but it has been pointed out by Dutoit and Friderich that the ethers and the ether salts are not polymerized solvents and that they yield solutions that do not conduct, or the conductivity of which is very slight; as in the case of ferric chloride solutions in phenyl-methyl ether. Ethyl carbonate does not yield solutions that conduct. The same is true for chloral solutions, and the esters of high carbon content yield solutions the conductivity of which is very slight. In the case of the substitution of chlorine for the ethoxy group in ethyl carbonate the number of spare valences is undoubtedly reduced, yet this product, ethyl chlorcarbonate, yields solutions that conduct well.

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[1] *Zeit. phys. Chem.*, **18**, 514; 1895; Ibid, **27**, 317; 1898; *Ber. chem. Ges. Berlin*, **30**, 163; 1897.

In compounds containing nitrogen, Brühl holds that the conductivity of their solutions is due to the extra valences of the nitrogen. He predicts that hydrazine will prove to yield solutions that conduct. It has been seen that phenylhydrazine does not yield solutions of the salts tested that conduct electricity; however, it still remains to be seen what hydrazine will do. He states that, in general, the dissociative power in the case of nitrogen compounds will vary with the nitrogen content, without being proportional to it, however; just as he claims it varies with the oxygen content of oxygen compounds. He further predicts that the anhydrous hydrocyanic acid, diazo compounds, and even unsaturated compounds of the elements other than oxygen, namely, PCl_3, $AsCl_3$, mercaptans and sulphur ethers, will possess dissociation power. Attention has been called to the fact, that when the CN group is substituted for hydrogen in ethyl acetate, the conductivity is materially increased. Nitriles do yield solutions that conduct very well. Contrary to Brühl's prediction, PCl_3 does not yield solutions that conduct; but in the case of $AsCl_3$ his prediction is confirmed. Werner found that solutions of cuprous chloride in methyl sulphide conduct very poorly. From the evidence we have at present it seems that the theory that the dissociative power of solvents is due to the unsaturated valences, that is, that the only solvents that yield solutions that conduct electricity, are unsaturated compounds, is not substantiated by the facts in many cases. Therefore the theory as promulgated by Brühl is untenable.

It is quite noticeable that a large number of the investigators of the properties of non-aqueous solutions, express the thought that there is manifested considerable influence between the dissolved substance and the solvent. This factor of the influence of the solvent upon the dissolved substance, is one that is no doubt of very great importance; and in the development of the electrolytic dissociation theory (which is based upon the behavior of aqueous solutions) the action of the solvent upon the dissolved substance has been entirely neglected. The opponents of the dissociation theory present this fact in a rather forcible manner.[1]

Fitzpatrick concludes from his investigation on the conductivity of alcoholic solutions that the action of the solvent upon the dissolved substance is a chemical one. He conceives the dissolved salt as decomposing and forming molecular groups in the solvent. Owing to the large excess of the solvent there will be a continual decomposition and recombination of these molecular groups. He cautions one against regarding the solvent as a medium in which the salt particles are suspended or as a dissociating agent. Wildermann[2], on the other hand, recognizes two kinds of dissociation — one, the electrolytic dissociation of the dissolved substance, and, the other, the dissociation of the larger molecular aggregates into smaller ones. For example, in a solution of KCl in water the following aggregates are assumed to exist: K_2Cl_2, KCl, $\overset{+}{K_2}Cl$, $\overset{-}{KCl_2}$, $\overset{+}{K}$ and $\overset{-}{Cl}$. He further maintains that solutions of all substances, whatever the solvent or concentration, undergo electrolytic dissociation.

Cattaneo[3] was impressed with the fact that the molecular conductivity is greatly influenced by the nature of the solvent employed. He was not able, however, to point out any direct relation existing between the various properties of the solvents which yield solutions that conduct. Konovaloff,[4] from his work on the amines, concludes that only those solvents that react chemically with the dissolved substance yield solutions that conduct. It is true that there are many solvents of this nature which do react with the dissolved substance, and yet which do not yield solutions that conduct electricity. Picric acid reacts with benzene but the resulting solution does not conduct electricity. Hence chemical combination of the dissolved substance with the solvent may take place and yet the solutions need not necessarily conduct. Werner has isolated and analyzed a large number of products of pyridine and piperidine, among those of other organic solvents, with salts of the heavy metals. From the boiling point determinations, the molecular weights of these salts seem to be very slightly influenced by their union with the solvent. This is analogous to the fact, that salts which crystallize from an aqueous solution with water of crystallization, yield the same molecular weights whether dissolved in the anhydrous form or with their water of crystallization. Werner perhaps sums up his idea best in the following manner: "Da nicht bezweifelt werden kann, dass in bestimmten organischen Lösungen hydratähnliche Additions-producte von Lösungsmittel und Metallsalz als beständige Verbindungen gelöst sind, so muss auch angenommen werden, dass bestimmte Hydrate in den wässerigen Lösungen enthalten sein können; wenn im letzterem Fall eine elektrolytische Dissoziation eintritt, so entstehen nicht Metallionen, sondern an deren Stelle treten ionisierte Metallwasserradikale." Carrara thinks that the union of solvent and dissolved substance accounts for the slight conductivity in certain cases. The low values for μ in the case of acetone solutions of HCl and LiCl he attributes to this fact.

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[1] Fitzgerald's "Helmholtz' Memorial Lecture," *Jour. Chem. Soc.* **69**, i, 885; 1896.

[2] *Ber. chem. Ges. Berlin* **26** 1773 and 1881; 1893.

[3] *Rend. Accad. Linc.*, II, 63 and 73; 1895. (Ref.) *Jour. Chem. Soc.* **72**, ii, 537; 1897.

[4] *Wied. Ann.*, **49**, 733; 1893.

It has been pointed out by Ciamician[1] that the dissociative power of a solvent depends principally upon its chemical strucure. That is, compounds of the same chemical type, for example, of the HOH type, yield solutions that conduct well. This is true in the case of alcoholic solutions, which are not the only class of compounds that possess dissociative power; as has already been pointed out. In general, however, if one member of a particular type of compounds (e. g. nitriles), yields solutions that conduct, it has been found that other members also possess this property; and if a member of some other type (e. g. hydrocarbons), is found not to yield solutions that conduct, other members do not possess dissociative power.

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[1] *Zeit. phys. Chem.*, 6, 403; 1890.

The data collected are as yet insufficient to show what the relation between solvent and dissolved substance must be in order to yield solutions that conduct electricity. Enough facts have been presented, however, to make it apparent that any theory that aims to explain the electrical conductivity of solutions in general, must take into consideration the influence of the solvent upon the dissolved substance. This subject is replete with interest; for closely connected with it is the true cause of the solubility of substances.

Carrara[1] states that the electrical conductivity of a solution depends upon (a) the dissociative power of the solvent and (b) on the electrical friction or friction between the solvent and the ions. This factor of electrolytic friction he obtains from Kohlrausch's formula $\mu_\infty = k\ (u + v)$, where k is a constant. This formula is based upon the fact that the conductivity in aqueous solutions is an additive property. Carrara himself has pointed out in the case of methyl alcoholic solutions, that the end value does not represent a condition of complete dissociation, but corresponds to an equilibrium between the dissociated, the undissociated and complex molecules. As evidence of this he points to the disagreement between the degree of dissociation when calculated from the boiling point and from the conductivity determinations. From the work of Dutoit and Friderich on the boiling point of acetone solutions, it appears that the degree of dissociation is very slight, since normal molecular weights were obtained; hence it would seem that the other factor, electrolytic friction, was the one remaining, according to Carrara, upon which the large conductivity of acetone solutions depends. It therefore appears evident that Carrara's idea cannot be accepted as the *sole* cause of electrolytic conductivity.

Dutoit and Friderich,[2] from the results of other investigators and from their own researches on the ketones and nitriles, conclude that; "la conductibilité des électrolytes dissous dans un dissolvant non polymérisé est null." The accuracy of this statement will become manifest when the following table is examined. In Table XXXVI are arranged the names of a number of solvents in the order of increasing coefficients of association. The names appear in the first column, the coefficient of association in the second. These values were mostly determined by Ramsay and Shields. (See Table I.) The third column contains the dielectric constants taken from Table I; and the fourth column contains the viscosity factors, η, as far as they could be obtained from the tables of Dutoit and Friderich and of Landolt and Börnstein. The last three columns contain the salts, the volume in liters in which our gram-molecule was dissolved, and the molecular conductivity at this particular concentration. That salt was usually chosen that gavé the largest value for μ.

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[1] Gazz. *Chem. Ital.*, I, 207-222; 1897; (Ref.) *Jour. Chem. Soc.*, **72**, ii, 471; 1897.

[2] Loc. cit.

Table XXXVI.

Solvent.	Coefficient of Association.	Dielectric constant. (Air = 1)	η	Salt.	v	μ
Quinoline	0.81			$Ag\,NO_3$	129.8	3.62
Paraldehyde	0.85			$Fe\,Cl_3$	575.5	17.00
Pyridine	0.93			NH_4I	2528.6	41.00
Nitrobenzene	0.93	32.19		$Fe\,Cl_3$	1451.9	20.80
Ethyl acetoaceate	0.96	15.70		$Fe\,Cl_3$	503.5	23.40
Benzonitrile	0.97	26.00		$Ag\,NO_3$	803.0	21.64
Benzaldehyde	0.97	14.48		$Fe\,Cl_3$	25.6	14.30
Phosphorus trichloride	1.02					
Aniline	1.05	7.50				
Acetophenone	1.05	16.40		$Fe\,Cl_3$	293.0	13.0
Carbon disulphide	1.07	2.61	0.00357			
Piperidine	1.08			$Ag\,NO_3$	4.24	0.37
Methyl-propyl ketone	1.11	16.75	0.0044	$Ag\,NO_3$	1074.0	59.5
Methyl-ethyl ketone	1.15	18.44	0.0041	$CNS.\,NH_4$	94.8	19.7
Butyronitrile	1.22		0.0056	$Ag\,NO_3$	150.4	32.1
Acetone	1.26	21.85	0.0031	KI	2315.2	153.2
Propionitrile	1.40		0.0040	$Ag\,NO_3$	250.0	38.86
Acetonitrile	1.60		0.0033	$Ag\,NO_3$	1141.4	159.3
Allyl alcohol	1.88	21.60	0.0130	$Fe\,Cl_3$	115.6	32.2
Propyl alcohol	2.25	20.45	0.0200	NaI	4495.5	174.7
Ethyl alcohol	2.74	25.70	0.0109	KI	∞	46.0
Methyl alcohol	3.43	32.65	0.0055	KI	∞	89.6
Water	3.60	78.00	0.0089	KI	∞	142.6

It will be observed that those solvents on the list down to and including benzaldehyde, are not polymerized liquids, according to their coefficients of association; and they all produce solutions that conduct electricity. Among these are benzaldehyde and paraldehyde, both of which yield solutions that conduct well. Benzonitrile, the coefficient of which, even according to Traube, shows virtually no polymerization, yields solutions that conduct very well; and according to Werner gives normal molecular weights by the boiling point method. Further, ethyl acetoacetate yields solutions that conduct very well; yet its molecules are not polymerized. It will also be noted that all of these solvents have relatively high dielectric constants. Solutions in nitrobenzene conduct; but according to Ramsay and Shields its molecules are not polymerized. Traube, however, gives a value of 1.47 for the coefficient of association of this substance. Of the organic bases quinoline yields solutions that conduct and shows the lowest degree of association of any of the solvents. Pyridine dissolves a large number of salts, and yields solutions that conduct; yet its molecules are not polymerized. It will be seen that the group of solvents whose coefficients of association are between 1 and 1.08 inclusive, thus indicating a slight degree of polymerization, yield solutions that conduct slightly, and Ramsay and Shields regard most of these as nonpolymerized liquids. Aniline yields solutions that conduct, particularly solutions of $AgNO_3$. Acetophenone solutions do not conduct very well; and those in piperidine conduct poorly; while phosphorus trichloride and carbon disulphide, whose molecules are slightly polymerized, do not yield solutions that conduct. The molecular conductivity of solutions of different solvents is not commensurate with the degree of polymerization of their molecules. This has already been pointed out in the case of methyl alcohol and water as well as propyl and methyl alcohols. The value of μ depends, however, to a great extent upon the salts chosen:—for example, the molecular conductivity of CdI_2 is virtually constant (11.7) in acetone, and in propionitrile it is 19.2, at dilution 512; while the conductivity of $AgNO_3$ is 30 in ethyl alcohol at dilution 41,000 liters, and 159 in acetonitrile at 1,141 liters.

The coefficients of association as determined by Ramsay and Shields have been employed in preference to those by Traube[1] because the method of the former has a better theoretical basis, and the results are more in accord with those of other investigators. Traube gives for the value of the coefficient of association for benzene 1.18, for toluene 1.08, ethylene chloride 1.46; and not any of these solvents yield solutions that conduct. Then he gives values for the esters that are very much in excess of the determinations of other investigators, whereas the values for the alcohols are very much less. For example, for methyl alcohol he gives as the coefficient of association 1.79; for ethyl alcohol 1.67; for propyl alcohol 1.55; for allyl alcohol 1.53, and for water 3.06. (Compare with the values given in Table I.)

Many compounds, whose molecules are polymerized, yield solutions that conduct, and there are solvents whose molecules are supposed to be polymerized that do not yield solutions that conduct; and if Traube's results be taken, a large number of examples could be given in addition to those cited above. It has also been pointed out that there are a considerable number of solvents, whose molecules are apparently not polymerized, yet whose solutions conduct well, — for example, benzonitile ethyl acetoacetate, etc.

From the considerations presented in the preceding, it appears that the theory as promulgated by Dutoit and Friderich, that only polymerized solvents yield solutions that conduct, is untenable.

Sometime before Dutoit and Friderich published their conclusions, Crompton[2] assigned a wider rôle to the associative property of liquids. He presents the view, that by means of this theory of association the anomalous results obtained, in the case of certain dissolved substances, electrolytes, by the boiling point, freezing point, and osmotic pressure determinations, can be easily explained; and aims to show that the electrolytic dissociation theory is not only unnecessary but in many respects inadequate. As has been previously noticed, Nernst[1] calls attention to the fact that solvents which have a high specific inductive capacity yield solutions that conduct; and he argues that the greater the dielectric constant, the greater is its power of dissociation. It has been pointed out above that no proportionality exists between the values of the dielectric constants of solvents and the molecular conductivity of their solutions. Crompton calls attention to the connection between the specific inductive capacity and the degree of association of solvents. This parallelism has also been pointed out by Abegg[2] who further observes that nitrobenzene, ethyl nitrate, and benzonitrile all have high dielectric constants; yet their association factor is unity. This, he thinks, fulfills the primary conditions of a self-dissociating substance. Crompton further states: "It is almost impossible to doubt that association plays an all-important part in determining the value of the specific inductive capacity of a liquid, and that if there is any connection between the specific inductive capacity and the power of forming electrolytes, it may be looked for rather in the fact that electrolytes are solutions of approximately monomolecular salts in an associated solvent, than in there being any peculiar 'dissociative power' attached to the solvent." From the experimental results given above it appears that it is a *fact*, that *all* solvents that yield solutions which conduct are *not associated* liquids.

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[1] *Ber. chem. Ges. Berlin*, **30**, 273–4; 1897.

[2] *Jour. Chem. Soc.*, **71**, ii, 925; 1897.

Crompton further aims to explain the conductivity of fused salts upon the dissociation of the associated molecules of the fused salt, wherein a small proportion of the salt is in the monomolecular condition. Abegg, however, shows that in many cases the melted salt has a higher dielectric constant than its "ice,"—for example water 78, ice 2.85;[3] and that in these fused salts the self-ionization or self-dissociation is very slight. He states that in about 100 liters of fused AgCl there is about one gram-molecule of AgCl completely dissociated. Kohlrausch[4] has shown that in about eleven million liters of water there is one gram of hydrogen ions; while in methyl alcohol Carrara[1] found one gram-molecule of methyl alcohol dissociated in about five and a half million liters. If water and methyl alcohol manifest such great dissociative power upon salts dissolved in them, why is it that they do not dissociate their own molecules to a greater extent?

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[1] Loc. cit.

[2] *Zeit. Electrochemie*, **5**, 48; 1899.

[3] Thwing.

[4] *Wied. Ann.*, **53**, 209; 1894.

CONCLUSION.

From the foregoing the following general statements may be made:

1. In methyl and ethyl alcoholic solutions limiting values for μ can usually be obtained. The salts of the heavy metals are apparently exceptions. In other solvents a limiting value is very seldom obtained.

2. Neither the dilution law of Ostwald nor that of Rudolphi holds in the case of alcoholic solutions. In other solvents (since the conductivity remains virtually constant in some cases with the increased dilution, while in other cases it decreases), it is very apparent that the above named laws do not hold. Then, too, since the value of μ_∞ cannot be obtained in the case of so many solvents, the validity of the dilution laws could not be tested.

3. The degrees of dissociation of the dissolved substances in non-aqueous solutions, as calculated from the boiling point or cryscopic determinations and from the conductivity measurements, show very great disagreement. No such agreement is manifest as is observed in the case of aqueous solutions.

4. Solvents that have a high dielectric constant, yield solutions that conduct the best. Some solvents, the dielectric constants of which are very low, give poorly conducting solutions. The molecular conductivity is not, however, proportional to the dielectric constant of the solvent.

5. Some associated solvents yield solutions that conduct electricity, whereas others do not. Some solvents whose molecules are not polymerized yield conducting solutions. The

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[1] Gazz, *Chem. Ital.*, **27**, I, 422; 1897; (Ref.) *Jour. Chem. Soc.*, **72**. ii, 473; 1897.

value of μ in those solutions that conduct, is not commensurate with the degree of association of the solvent.

6. The molecular conductivity, in general, increases with the dilution; but in several cases the conductivity decreases with the successive dilutions.

7. The molecular conductivity usually increases with the temperature; but not proportionately. In some cases it remains virtually constant with increase of temperature, while in others it decreases. The changes in viscosity accompanying a varying temperature have not been determined.

8. The conductivity of electrolytes depends very much upon the nature of the solvent employed. No rigid classification can be made; but, in general, solutions in the hydrocarbons and their halogen substitution products do not conduct. Alcoholic solutions conduct well and the conductivity, in general, decreases with the increase of the carbon content. Solutions in esters conduct, but those of high carbon content usually yield solutions that conduct very poorly. The ketones and the aldehydes yield solutions that conduct well. Of the nitrogen compounds ammonium and ammonia substitution products, or amines, conduct The nitriles of both the aliphatic and aromatic series yield conducting solutions; and of the organic bases, pyridine and quinoline come under this same category.

9. The dissociation theory as promulgated for the explanation of the electrical conductivity of aqueous solutions, apparently cannot be applied in its present form to explain the conductivity in non-aqueous solutions. It further appears that the auxiliary theories, which are based upon the specific inductive capacity, the polymerization of the molecules, and the self-ionization of the solvent, are not sufficient to explain satisfactorily the facts that have been accumulated. Notwithstanding the work that has been done, the data at hand are as yet insufficient for the formulation of a theory by means of which a satisfactory explanation can be given of the phenomenon of electrical conductivity of solutions in general.

This investigation was made in the Laboratory of Physical Chemistry of the University of Wisconsin. It was undertaken at the suggestion of Professor Kahlenberg and carried on under his supervision. I am under many obligations to him for his valuable suggestions and assistance and I take this means of acknowledging the same.

A portion of the results of the earlier part of the work has previously been published by Professor Kahlenberg and myself jointly in a preliminary paper in the *Journal of Physical Chemistry* **3**, 12, 1899. For the sake of completeness the results have also been incorporated in the present article.

Madison, Wis., April, 1899.

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